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THE ADSORPTION OF ARGON AND OXYGEN ON SILVER MORDENITE

by
Bernard E. Wilkerson, 1Lt, USAF

M.S.Ch.E.
The Ohio State University
1990

THESIS ABSTRACT

The maximum oxygen purity from a conventional pressure swing adsorption system is 95%, due to difficulty in separating argon and oxygen using 5A or 13X zeolites. Silver mordenite was studied as an alternative to the conventional adsorbents. Silver mordenite was prepared at three different silver concentrations, and adsorption isotherms were measured at 0, 30, 60 and 90 degrees C. Based on these isotherms, and other properties, recovery using a potential PSA process was predicted. It appears that a high silver concentration is necessary to produce pure oxygen using PSA. Due to kinetic constraints at low temperatures and poorer equilibrium at high temperatures, the optimum operating temperature is likely to be near 30 C.

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Miller, G.W., and Theis, C.F., "Secondary Oxygen Purifier for Molecular Sieve Oxygen Concentrator," SAFE Journal, 19 (1989).

Knaebel, K.S., and Hill, F.B., "Pressure Swing Adsorption: Development of an Equilibrium Theory for Gas Separations," Chemical Engineering Science, 40 (1985).

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Kent S. Knaebel

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THE ADSORPTION OF ARGON AND OXYGEN ON SILVER MORDENITE

A Thesis

Presented in Partial Fulfillment of the Requirements for

the degree Master of Science in the

Graduate School of the Ohio State University

by

Bernard E. Wilkerson, B. S.

* * * *

The Ohio State University

1990

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NOMENCLATURE

Acs	Cross sectional area
C	Concentration
K	Constant in the Langmuir equation. Equal to the Henry's Law slope at low pressures
Hst	Isosteric heat of adsorption
L	Bed length
m1	Defined by equation (10). The slope of the more strongly adsorbed component when y=0
m2	Defined by equation (11). The chord of the more strongly adsorbed isotherm between y=0 and the feed concentration and pressure
m3	Defined by equation (12). The chord of the less strongly adsorbed isotherm between the concentration of the high pressure product and the concentration of the high pressure feed
N_i	The number of moles for the ith stage of a PSA cycle
n_i cell(s)	The number of moles of gas in the isotherm
n	Number of data points
P	Absolute pressure (psia or atm)
Ph	High pressure (atm)
Pl	Low pressure (atm)
Pai	The pressure in cell A at step i
Peqi	The pressure in the system at step i
p	Number of free parameters

R	Recovery, as defined by equation (14). Also the gas constant
r	Constant in the Langmuir equation
T	Temperature
V	Volume in cell A or B
wt	The weight of the adsorbent in cell B
y	The mole fraction of the gas at a given step
Y	Data fit in a model
Y	Prediction of Y using model

Greek symbols:

β_0	Dilute solution selectivity
β_{A0}	Defined by equation (6)
ϵ	Void fraction
p	Density
θ	Defined in equations (7)-(9)
σ	Standard error of estimate. Defined in equation (21)

Subscripts:

A	Cell A. Also, the more strongly adsorbed component
B	Cell B. Also, the less strongly adsorbed component
b	Bulk
eq	Equilibrium for the isotherm system
F	Feed step

H	High pressure feed step
HP	High pressure product
i	Property at a given step
L	Purge step
p	Particle
PR	Pressurization step
s	Solid

CHAPTER I

INTRODUCTION

Oxygen is produced by pressure swing adsorption (PSA) for use in many applications, including waste-treatment plants, steel manufacturing, in-home patient care and on certain military aircraft. The first two applications require only an oxygen-enriched feed stream, while the last two require high purity oxygen [1,2].

PSA is a process whereby a feed stream containing two or more gases is compressed and passed through a column packed with an adsorbent. In an equilibrium separation, the components that appear as byproducts are adsorbed more strongly, while the purified product component is adsorbed less strongly. The pressure is cycled to allow the more strongly adsorbed components to be vented, and the adsorbent bed is regenerated for the next feed cycle [3] (for a description of the history and development of PSA, see Yang [3] or Collins [4]). In the case of oxygen production using zeolite 5A or 13X, for example [5], air is compressed as the feed stream. Nitrogen is more strongly adsorbed, thus producing a stream of enriched or purified oxygen. The third major component of air, argon, is similar in size to

oxygen, and is non-polar, like oxygen, and thus adsorbs similarly to oxygen. Because of this similarity, most of the argon comes off with oxygen in the product stream. This limits the oxygen purity to about 95%, with the remaining 5% being argon [6].

For many applications, this is sufficient purity. Steel manufacturing, for example, uses enriched streams of less than 40% oxygen [2]. But other applications, such as the generation of oxygen on-board military aircraft, can require oxygen concentrations greater than 95%. Currently, such systems require a back-up of 99.5% oxygen [6]. If an adsorbent that could adsorb argon more strongly than oxygen were incorporated into a PSA system to treat the oxygen and argon product mentioned above, it would eliminate the need for such a back-up, and could theoretically produce oxygen concentrated to 99.99%. To obtain oxygen of this purity presently requires cryogenic means, which are not cost effective compared to PSA at production rates of lower than 20 to 30 metric tons/day [1,3].

In 1974, Wolf and Koenig [7] discovered, using gas chromatographic methods, that Na^+-mordenite showed a selectivity between argon and oxygen at room temperature. They found that argon would diffuse through the adsorbent faster than oxygen and nitrogen; hence a kinetic based, rather than equilibrium based, separation. Wolf and Koenig [8] also noted that silver ion-exchanged forms of some

zeolites had been used to separate argon and oxygen, presumably also using gas chromatographic methods. In 1983, Boniface [9] also used gas chromatography to find a zeolite that would selectively adsorb more oxygen than argon, thus allowing argon to be separated from an oxygen/argon mixture. Among the many zeolites tested, Ag^+-mordenite, or more simply, silver mordenite, showed the reverse selectivity of what he desired. That is, it selectively adsorbed more argon than oxygen.

Silver mordenite is the ion-exchanged form of sodium mordenite. Sodium mordenite, in its natural form, was first characterized by Meier [10]. It is composed of a framework of tetrahedral unit cells having an ideal composition of $Na_8[Al_8Si_{40}O_{96}]$. The aluminosilicate framework forms a series of parallel linear channels with aperture dimensions of about 6.7 X 7.0 Angstroms, lined with side pockets having openings of about 3.9 Angstroms. In the silver mordenite form, Ag^+ ions exchange directly with the Na^+ ions in the lattice. There are several methods for performing this exchange, which are described later.

The purpose of this work is to determine experimentally the feasibility of using silver mordenite as an adsorbent in a PSA process to purify oxygen from a feed stream of 95% oxygen and 5% argon. According to the equilibrium theories of Knaebel and Hill [11] and Kayser and Knaebel [12], it is necessary to determine the void fraction of an adsorbent,

and the equilibrium isotherms of the pure component gases on the adsorbent, to determine the feasibility of using the adsorbent in a given PSA process. Thus, the void fractions of silver mordenite at different silver concentrations and the pure component equilibrium isotherms of argon and oxygen on silver mordenite at the same concentrations and at various temperatures were measured.

CHAPTER II

THEORY

Pressure swing adsorption is typically a four step process, although there are some variations [4]. Two columns are generally used, one operating 180 degrees out of phase with the other. The columns are packed with an adsorbent that selectively adsorbs one component more strongly than the other. A system of valves and compressors is attached to the columns to allow for the pressurization and de-pressurization steps described in the following paragraphs.

The four steps of a typical PSA process are:

1) Feed

2) Blowdown

3) Purge

4) Pressurization with either feed or product.

Only the case of pressurization with product will be discussed here.

In the first step, pressurized feed enters the column, which has been pressurized with the pure, less strongly adsorbed component. As the feed passes through the column, the more strongly adsorbed component is selectively taken

up. Thus, at the other end of the column, a continuous stream of purified, less strongly adsorbed component is taken off. As the bed reaches capacity, the product stream is closed off, and the blowdown step begins. The pressurized column is vented to decrease the pressure. In the purge step, a portion of the product flows through the column, countercurrent to the feed step, to regenerate the adsorbent bed. A valve at the feed end is closed, and the purified product pressurizes the column in the pressurization step. This completes one PSA cycle. The second column operates 180 degrees out of phase with this cycle, as noted earlier, thus allowing for a continuous feed stream (that alternates between columns) and a continuous product stream [11].

An equilibrium theory that models this process has been derived by Knaebel and Hill [11] and verified by Kayser and Knaebel [13]. The constraints and assumptions of the theory are:

1) Binary, ideal gas mixture.

2) Local equilibrium between gas and solid phases.

3) Linear, uncoupled equilibrium adsorption isotherms.

4) Negligible axial dispersion.

5) Negligible axial pressure gradients.

6) Constant pressure during the feed and purge steps.

7) Isothermal operation.

8) No radial dependence in velocity or composition.

The third assumption of this theory was modified to extend to the case of nonlinear, uncoupled, equilibrium adsorption isotherms by Kayser and Knaebel [12]. This modification to the original theory applies to this work since the isotherms of argon and oxygen on silver mordenite are nonlinear.

From Kayser and Knaebel [12], the analytical solution to the material balances on each PSA step for nonlinear isotherms are

$$N_{PR} = AcsL(\epsilon((Ph/RT)-(Pl/RT))+(1-\epsilon)(f_{BH}-f_{BL})) \tag{1}$$

for the number of moles of product required for pressurization,

$$N_L = AcsL\epsilon Pl/\beta_{A0}RT \tag{2}$$

for the number of product moles required for the purge step,

$$N_{HP} = N_H(1+(\theta-1)y_{AF}) \tag{3}$$

for the total number of product moles, and

$$N_H = AcsL\epsilon/\theta_A RT \tag{4}$$

for the number of moles of the product component originally in the feed, where

$$f_{BH} = f_B(Ph \ y_B/RT) \quad \text{and} \quad f_{BL} = f_B(Pl \ y_B/RT) \tag{5}$$

and

$$\beta_{A0} = 1/(1+((1-\epsilon)/\epsilon)m1) \tag{6}.$$

Also,

$$\theta = \theta_A/\theta_B \tag{7}$$

where

$$\theta_A = 1/(1+((1-\epsilon)/\epsilon)m2) \tag{8}$$

and

$$\theta_B = 1/(1+((1-\epsilon)/\epsilon)m3) \tag{9}$$

and,

$$m1 = f'|_{ya=0} \tag{10},$$

$$m2 = f_A(Ph\ y_{AF}/RT)/(Ph\ y_{AF}/RT) \tag{11}$$

and

$$m3 = \frac{f_B(Ph\ y_{BHP}/RT)-f_B(Ph\ y_{BF}/RT)}{(Ph\ y_{BHP}/RT)-(Ph\ y_{BF}/RT)} \tag{12}.$$

Now, a significant measure of performance of a PSA operation is the pure component product recovery, which is the ratio of the number of moles of less strongly adsorbed component that comes off as net product to the number of moles of same component that entered as feed, and can be expressed as [11]

$$R = (N_{HP}-N_L-N_{PR})/((1-y_{AF})N_H) \tag{13}.$$

Substituting equations (1), (2), (3), and (4) into (13) leaves

$$R = \frac{[((1+(\theta-1)y_{AF})/\theta_A)+(Ph/Pl)((\beta_{A0}-1)/\beta_{A0})-1-((1-\epsilon)/\epsilon)(RT/Ph)(f_{BH}-F_{BL})]}{[(1-y_{AF})/\theta_A]} \tag{14}.$$

Recovery can then be calculated by knowing the pure component adsorption equilibrium isotherms, the void fraction, the feed and product concentrations, the high and low pressures, and the isothermal temperature. This can be done on a theoretical basis by assuming operating conditions, such as the concentrations and pressures, experimentally determining the isotherms at the operating

condition temperature, and finding the void fraction from the particle and bulk densities.

To find the void fraction, we start with the relationship of the bulk density to the particle density

$$p_b = (1-\epsilon)p_p \qquad (15),$$

which can be rearranged so,

$$\epsilon = 1-(p_b/p_p) \qquad (16)$$

to give an explicit expression for void fraction.

The experimental procedure for determining the pure component equilibrium adsorption isotherms will be discussed in the next chapter, however the material balances involved in the analysis are given here. An amount of pure gas is admitted into an empty chamber submerged in an isothermal bath and the pressure is measured. Using the ideal gas law relationship, the number of moles added to the chamber is

$$n_{ai} = ((Pa_i-Peq_{i-1})V_A)/RT \qquad (17).$$

A valve is opened that allows the gas from the first chamber to enter a second chamber containing the adsorbent. The valve is left open to allow the gas to come to equilibrium in both chambers. The total number of non-adsorbed moles in the system is found, again using the ideal gas law relationship, by

$$n_{eqi} = ((Peq_i-Peq_{i-1})(V_A+V_B-wt/p_p))/RT \qquad (18).$$

The number of moles adsorbed is equal to the number of moles admitted to the system minus the number of moles not

adsorbed, or in general form

$$n_i = ((Pa_i - Peq_{i-1})V_A) - (Peq_i - Peq_{i-1})(V_A + V_B - wt/p_n))/RT \quad (19).$$

The number of moles adsorbed are plotted versus the number of moles not adsorbed to obtain the isotherm curve. This curve can then be fitted to an adsorption isotherm equation, such as Henry's Law, for straight line isotherms, or Langmuir's equation, which reduces to Henry's Law at low pressures. The Langmuir equation is

$$n_i = K(P_i y/RT)/(1 + r(P_i y/RT)) \quad (20).$$

As shown later, no experiments actually reached saturation so the estimate of r may be unreliable [14]. Empirically, however, the fits were excellent.

For nonlinear models, a useful estimate of the reliability of the fit is the standard error of estimate [15]

$$\sigma = [\frac{(Y_i - Y_i)^2}{(n-p-1)}]^{1/2} \quad (21).$$

This is useful only for comparisons between fits, however, as its magnitude is dependent upon the values of the dependent variable.

As a further characterization of the adsorbent, it is possible to follow a procedure similar to the isotherm measurement to determine the solid, or crystalline, density, p_s. Helium is used because it is small enough to penetrate even the side cages of the mordenite. Using a similar material balance as in equation (19), the solid volume of

the adsorbent can be solved for:

$$V_{solid} = V_B - V_A((Pa_i - Peq_i)/(Peq_i - Peq_{i-1}))$$ (22).

Knowing the weight of the adsorbent in cell B, one can then determine the solid density.

With the isotherm data calculated, the isosteric heat of adsorption can also be found using the following equation [16]:

$$\Delta Hst = -R[\partial \ln P / \partial (1/T)]_c$$ (23).

CHAPTER III

EXPERIMENTAL METHODS

A. Preparing Silver Mordenite

The mordenite used in this work was Union Carbide Molecular Sieve Type AW300, small port, synthetic, sodium mordenite. Two methods were used for converting it from sodium ion form to silver ion form:

1) Dripping 0.2N $AgNO_3$ through a heated column filled with sodium mordenite [17].

2) Stirring the sodium mordenite in a beaker of 0.2N $AgNO_3$ solution for 2 hours, then filtering. For a high percent exchange, this must be repeated 3 to 4 times [17].

Method 1 was used for obtaining a high percent exchanged silver mordenite and method 2 was used without repetition to obtain a low percentage exchange.

A.1. Method 1

The procedure followed for method 1 was [17]:

1) Dry about 100g of sodium mordenite at 110 C in an oven for two hours.

2) Weigh.

3) Spread the mordenite out in a shallow tray.

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4) Spray with distilled water to hydrate the mordenite. Mordenite generates a large amount of heat when water is adsorbed [18].

5) Place the hydrated mordenite into a column already containing distilled water.

6) Heat the column to near boiling, and back flush with heated, distilled water for 20 minutes to remove entrained air. See Figure 1.

7) Maintaining the temperature between 80 and 90 C, drip in the silver nitrate feed (see below for feed preparation). The flow rate should be such that the feed will drip into the column for about 16 hours. See Figure 2.

8) Wash the exchanged mordenite with 5 to 10 bed volumes of heated, distilled water.

9) Drain the mordenite, and dry it in an oven at 90 C for several hours.

A.2. Method 2

To prepare a low percent exchanged silver mordenite, method 2 is used, but with a different feed concentration. A silver nitrate solution with a concentration of about 0.09N is prepared as described below, using 9g $AgNO_3$ mixed with 600ml distilled water. To do the exchange, steps (1) through (4) of method 1 are carried out, and then the following steps [17].

Excess
Water
Run-off

Fluidized
Adsorbent
Particles

Hot
Water
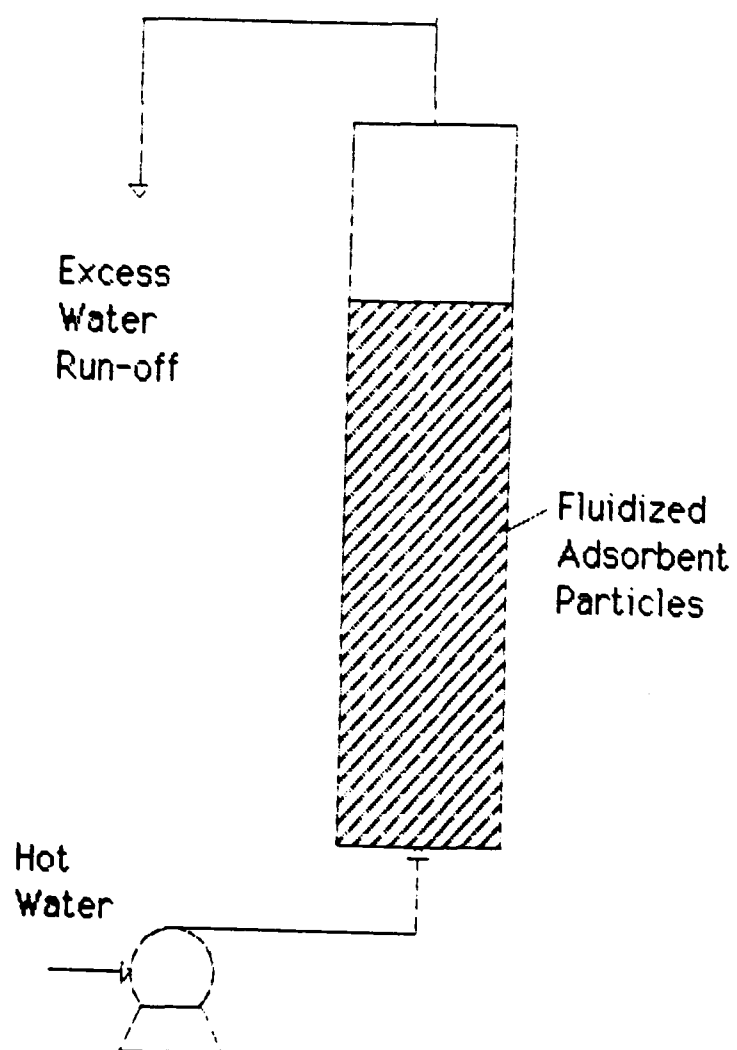
Figure 1: Back Flush System

Silver
Nitrate
Feed

Adsorbent
Particles

Effluent
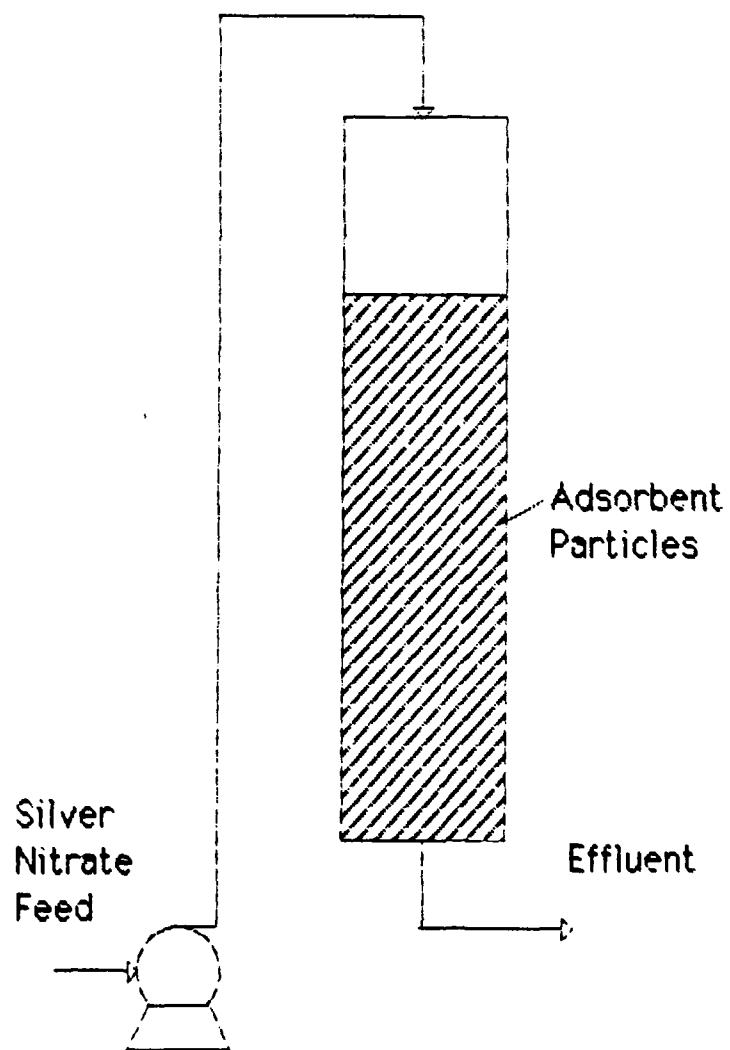
Figure 2:   Column Exchange System

5) Place the hydrated mordenite into a heated, glass vessel, with sufficient water to slurry the mordenite. See Figure 3.

6) Boil the water, and stir the mordenite vigorously to remove any entrained air.

7) Remove some of the water, being careful not to allow the water level to fall below the mordenite level, exposing mordenite to air.

8) Add the low concentration $AgNO_3$ feed.

9) Stir the contents of the vessel with an agitator for 2 hours at 90 C.

10) Drain the exchanged mordenite, and place it on a Buchner funnel.

11) Filter 1.5 to 2 liters of heated, distilled water through the silver mordenite to wash it.

12) Drain the mordenite, and dry it in an oven at 90 C for several hours.

A.3. Regeneration

By whichever method the silver mordenite is prepared, it must be thoroughly regenerated to prepare it for use in adsorption. The regeneration procedure is:

1) Place the mordenite into a stainless steel column, and heat to between 350 and 400 C, taking care not to exceed 400 C.
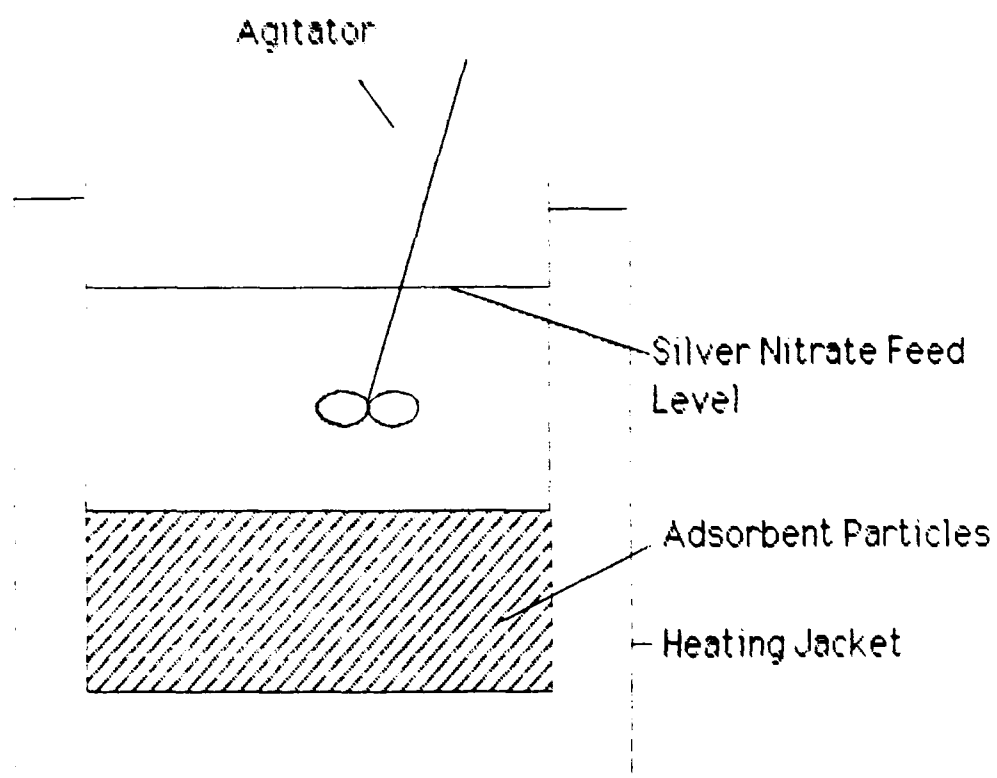
Figure 3: Batch Exchange System

2) With a low-vacuum pump, evacuate the column to about 2 psia for several hours.

3) Attach a high-vacuum pump (protected by a column filled with an adsorbent to take up any moisture evolved by the mordenite) and, with a temperature still in the range of 350-400 C, evacuate the column to near vacuum for at least 12 hours.

A.4. Preparing the Feed

The feed solution of silver nitrate is prepared by the method of Swift and Butler [19].

1) Place approximately 34g of crystalline $AgNO_3$ into a weighing glass.

2) Dry at 110 C for two hours. There must be no paper or any other material that may char in the oven, as this will cause the silver nitrate to reduce, making it unusable.

3) Allow the weighing bottle and its contents to cool in a desiccator. The bottle should be a brown glass bottle, or covered in tin foil, to reduce the exposure to light. Light will also reduce the silver nitrate. After drying, the crystals should be very white. Discoloration means that some reduction has taken place.

4) Weigh the bottle and crystals.

5) Place the crystals in a 1L graduated cylinder.

6) Weigh the empty bottle, and determine the weight of $AgNO_3$ added by difference.

7) Add distilled water to the cylinder to bring the total volume to 1 liter.

8) The normality of the solution can be calculated. It should be approximately 0.2N.

9) The solution should be stored in a brown glass or covered glass bottle. It is advisable not to store it for very long, but to use it as soon as possible.

The calculated normality can be quickly checked by performing a clear point titration with NaCl, as described in Swift and Butler [19].

To achieve a high percent exchange, a 3 to 4 fold amount of silver nitrate is required [17]. The silver ions exchange one for one with sodium ions on the mordenite framework. Sodium ions comprise 6.01 wt% in sodium mordenite (excluding inert binder, which can be 10 to 20% by weight). 100g of sodium mordenite (ignoring the binder for this calculation) thus contain 0.261 gmol of sodium ion. For a theoretical 100% exchange with silver ions, the same amount of silver ions (and thus silver nitrate), must be used. This works out to be 44.4g of $AgNO_3$. A four-fold amount of silver nitrate is about 176g, which is a little more than 5 liters of 0.2N $AgNO_3$ solution.

The pH of the solution must be adjusted to about 4 [17]. This is accomplished by adding 7.6 ml of 0.1 WF HNO_3.

During operation, the feed tank and column are covered in tin foil to shield the silver nitrate from light.

B.   Void Fraction Determination

As mentioned in an earlier chapter, it is necessary to find the void fraction, ϵ, of the adsorbent. This is done using equation (16) and finding the particle and bulk densities (p_p and p_b, respectively) experimentally. These densities are found using the method of Ball [20]. To find the bulk density:

1)   Weigh a graduated cylinder.

2)   Add a small amount of the adsorbent, shaking it slightly to allow it to settle.

3)   Find the weight by difference, and divide by the indicated volume to find the density.

To find the particle density:

1)   Weigh a 50ml volumetric flask.

2)   Add about 25g of adsorbent, and find the weight by difference.

3)   Add cyclohexane and gently agitate to release air.

4)   Allow to settle, then add cyclohexane to the 50ml mark.

5)   Weigh, and find the weight of cyclohexane by difference. From this weight, and using the density of cyclohexane, the volume of cyclohexane added can be found.

The density of cyclohexane was experimentally determined to be 0.774 g/ml, which agreed with the literature value [15].

6) The volume of cyclohexane is subtracted from 50ml, giving the volume of the adsorbent particles. Knowing the mass, the particle density can be calculated. Note that the cyclohexane penetrates the larger micropores (6.7 X 7.0 Angstroms), but not the smaller side pockets (3.9 Angstrom apertures). Thus the volume determined is that of the solid and of the side pockets.

C.   Isotherm Determination

To determine the pure component equilibrium adsorption isotherms, the apparatus shown in Figure 4 is used. A vacuum pump is attached, and both valves are opened. The vacuum pump is used to evacuate the system, which is then held under vacuum for at least 12 hours. With V1 closed, and V2 open, the system is allowed to come to the desired temperature in an isothermal bath. The starting pressure (near vacuum) is noted, and becomes Peq_0, then V2 is closed. The procedure below is followed:

1) With V2 closed, admit some gas into (or, in the case of a desorption point, release some gas from) cell 1.

2) Allow to come to thermal equilibrium, i.e., no change in pressure with respect to time, and record the pressure as Pa.

3) Open V2.
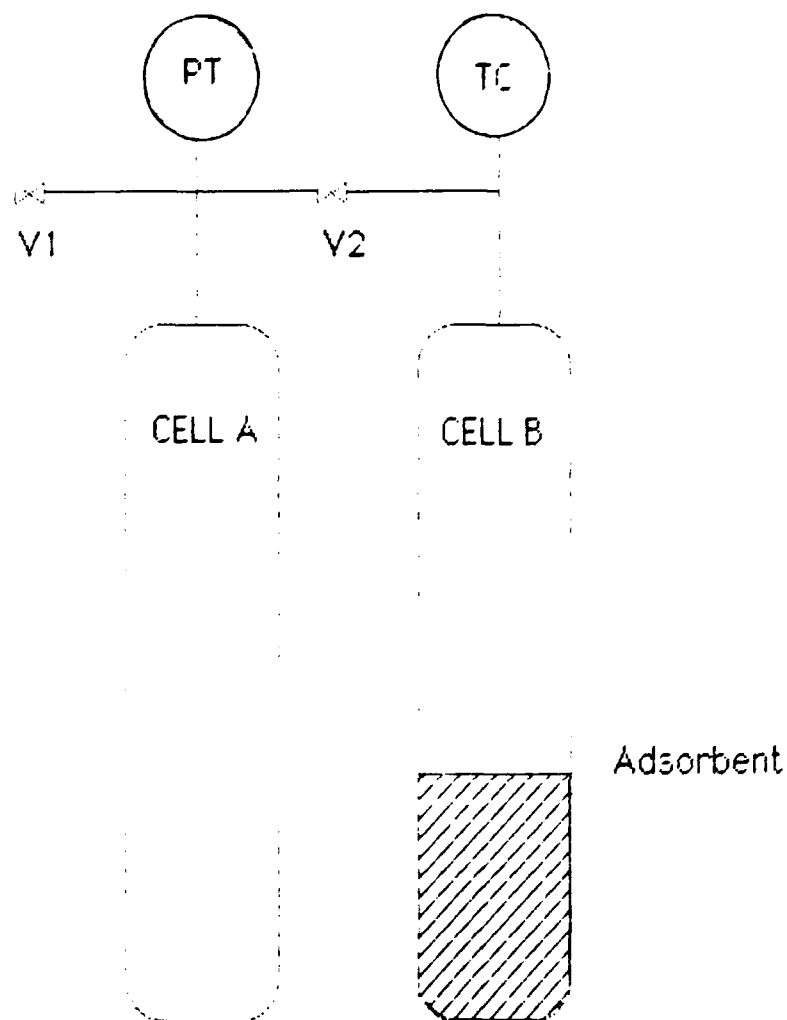
Figure 4:   Isotherm Apparatus

4) Allow to come to equilibrium, and record the pressure as Peq.

5) Close V2. Repeat procedure for as many points as desired.

To ensure system integrity and that the system has come to equilibrium with each step, it is necessary to do several desorption points. There should be no hysteresis evident in the plot of the isotherm data [20]. To calculate the adsorbed and non-adsorbed moles for each point, equation (19) is used.

Using helium, steps 1 through 5 can be followed as outlined above to determine the solid density of the adsorbent. Equation (22) is used to calculate the solid volume, and the density is then found knowing the weight of the adsorbent.

CHAPTER IV

ANALYSIS OF RESULTS

A.   Introduction

This chapter presents the results of the experiments described in Chapter III, interpreted using the methods outlined in Chapter II.

B.   Void Fraction Results

Table 1 shows the results of the void fraction determination. The densities increase with increasing silver concentration, which is expected, since the silver is heavier than sodium. The void fraction is also slightly higher for the silver exchanged mordenite than the non-exchanged form. The particle density is important in the calculation of the adsorption isotherms, and the void fraction is used in calculating the theoretical recovery. Each value in Table 1 is an average of several trials. The trial data are in Appendix A.

C.   Isotherm Results

Table 2 is a summary of the Langmuir equation constants (from equation (20)) for each adsorbent at each temperature.

Table 1: Densities and Void Fractions

Adsorbent	p_b (g/cm^3)	p_p (g/cm^3)	p_s (g/cm^3)	ϵ
Silver Mordenite	0.8926	2.3645	2.7692	0.6225
Batch Exchanged (low %) Silver Mordenite	0.8383	2.1815	2.5794	0.6157
Sodium Mordenite	0.8306	2.0996	2.4487	0.6044

Table 2: Summary of Langmuir Constants

Langmuir constants, A - Ar, B - O_2

$K \ [=] \ (mol/m^3)(solid)/(mol/m^3)(gas)$

$r \ [=] \ (m^3/mol)(gas)$

Adsorbent

T(deg C)	K_A	r_A	K_B	r_B
Silver Mordenite				
0	14.1824	0.597161D-02	12.5382	0.521006D-02
30	8.44450	0.372051D-02	7.35140	0.306207D-02
60	4.98934	0.241958D-02	4.25105	0.187029D-02
90	2.68983	0.150029D-02	2.22087	0.952117D-03
Sodium Mordenite				
0	6.19725	0.282193D-02	5.94683	0.257768D-02
9.5	5.01313	0.223639D-02	4.92165	0.219972D-02
30	3.41589	0.205224D-02	3.56520	0.209385D-02
60	2.17725	0.122378D-02	2.07370	0.106641D-02
89	1.37579	0.706398D-03	1.36144	0.737007D-03
Batch exchanged Silver Mordenite				
0	4.68081	0.744564D-03	9.09396	0.299056D-02
30	5.20958	0.212379D-02	5.15833	0.211539D-02
60	3.43117	0.171994D-02	3.21696	0.144431D-02
89	2.18766	0.111527D-02	2.05187	0.995029D-03

These constants were found from the isotherm data using a
computer program that uses a modification of the sequential
complex search technique [21]. None of the experiments
reached saturation, so there is no ideal, localized
adsorption. Thus the values for r may be unreliable beyond
their use as a fit for the data [14]. Empirically, however,
the data fits were excellent, and the results are valid over
a wide range of operating conditions. At pressures greater
than, say, 15-20 atm, though, the results may not be as
valid. A summary of the raw data, calculated isotherm
points, Langmuir constants and the standard error of
estimate for each adsorbate-adsorbent system at each
temperature can be found in Appendix B. The isotherm
points, along with the curves calculated from equation (20),
are plotted for each system in Figures 5 to 17. As can be
seen from the first few plots, the absolute adsorption
decreases dramatically with increasing temperature.
However, the time it takes for the adsorption process to
come to equilibrium at the lower temperatures is markedly
different than at the higher ones. For all adsorbents, it
typically took 6-12 hours for the process to reach
equilibrium with each adsorption step at 0 C. At 30 C, this
improved to only 1 hour, and at 90 C, only a half an hour
was required for the adsorption step to reach equilibrium.
The slow kinetics at low temperatures could preclude the use
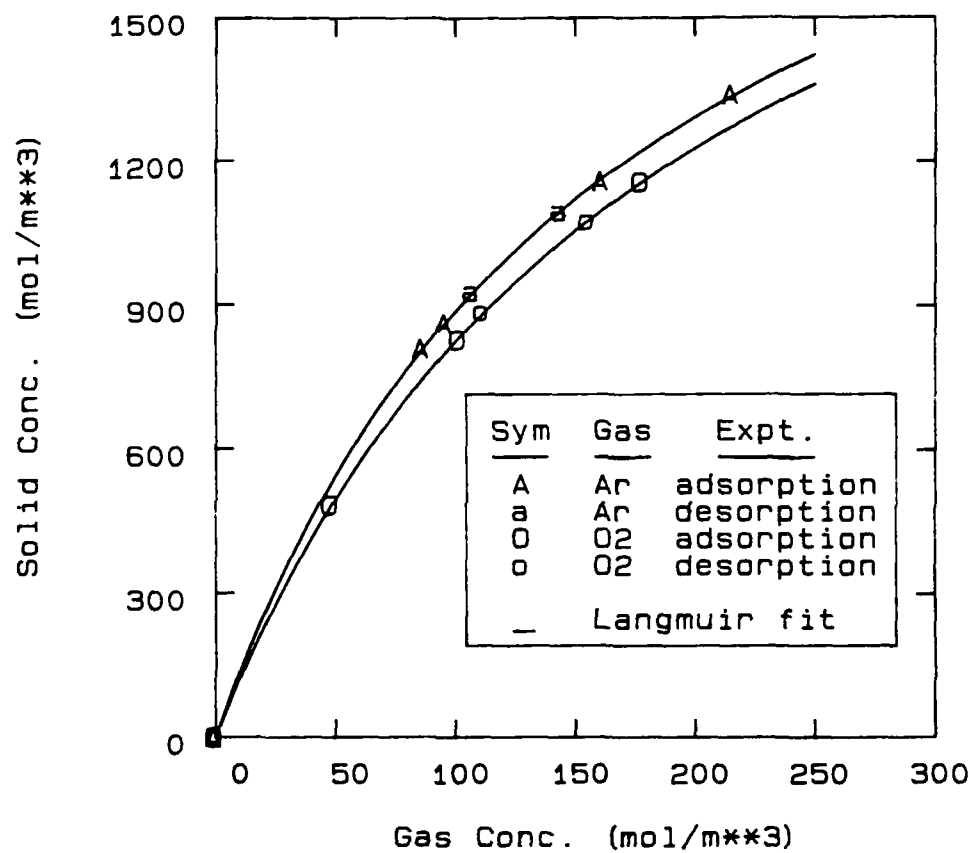
Figure 5. Adsorption of Argon and Oxygen on Silver
Mordenite at 0 C
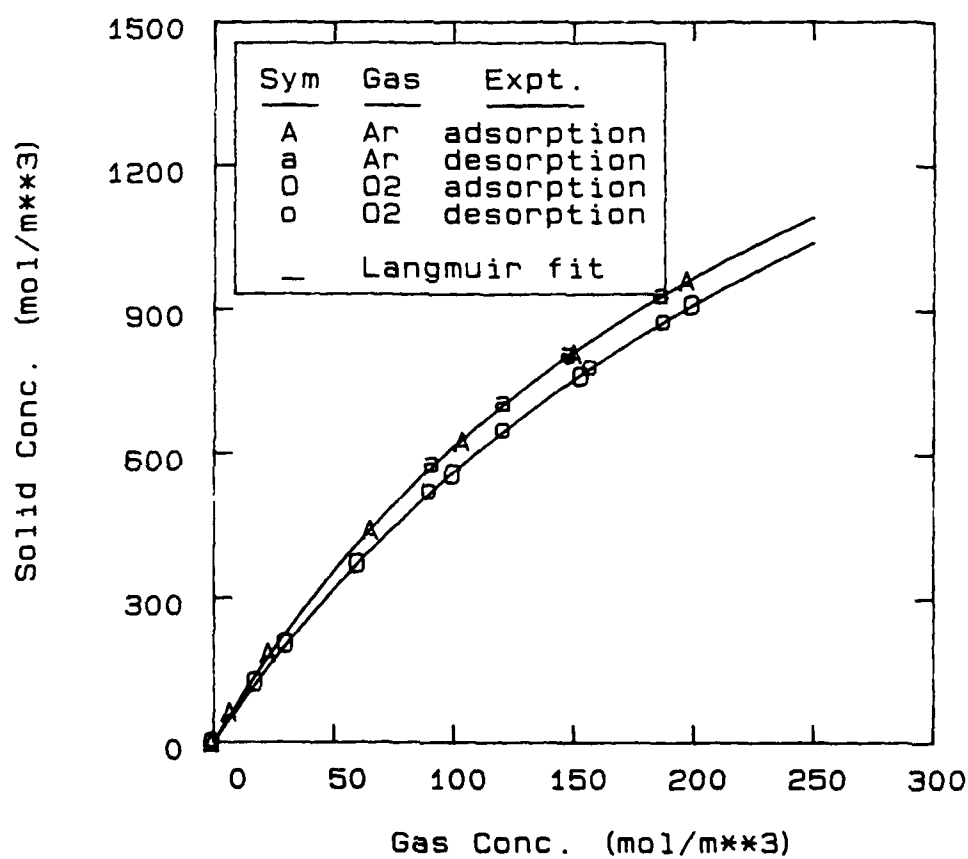
Figure 6. Adsorption of Argon and Oxygen on
Silver Mordenite at 30 C
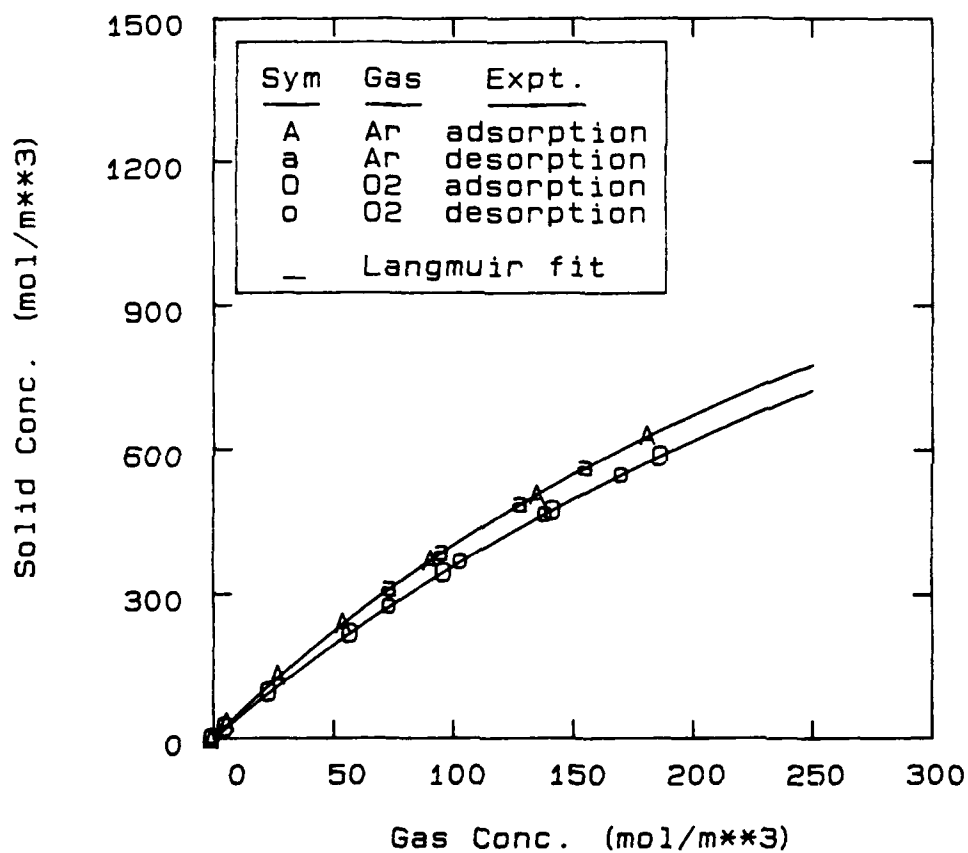
Figure 7. Adsorption of Argon and Oxygen on
Silver Mordenite at 60 C
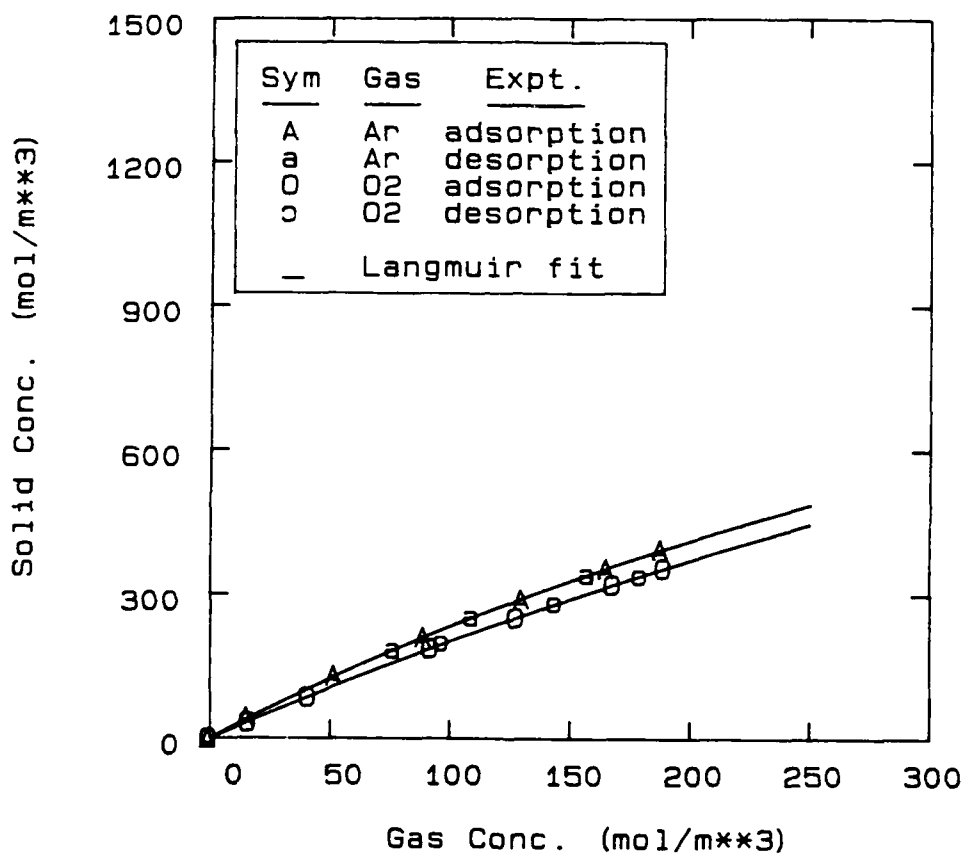
Figure 8. Adsorption of Argon and Oxygen on
Silver Mordenite at 90 C
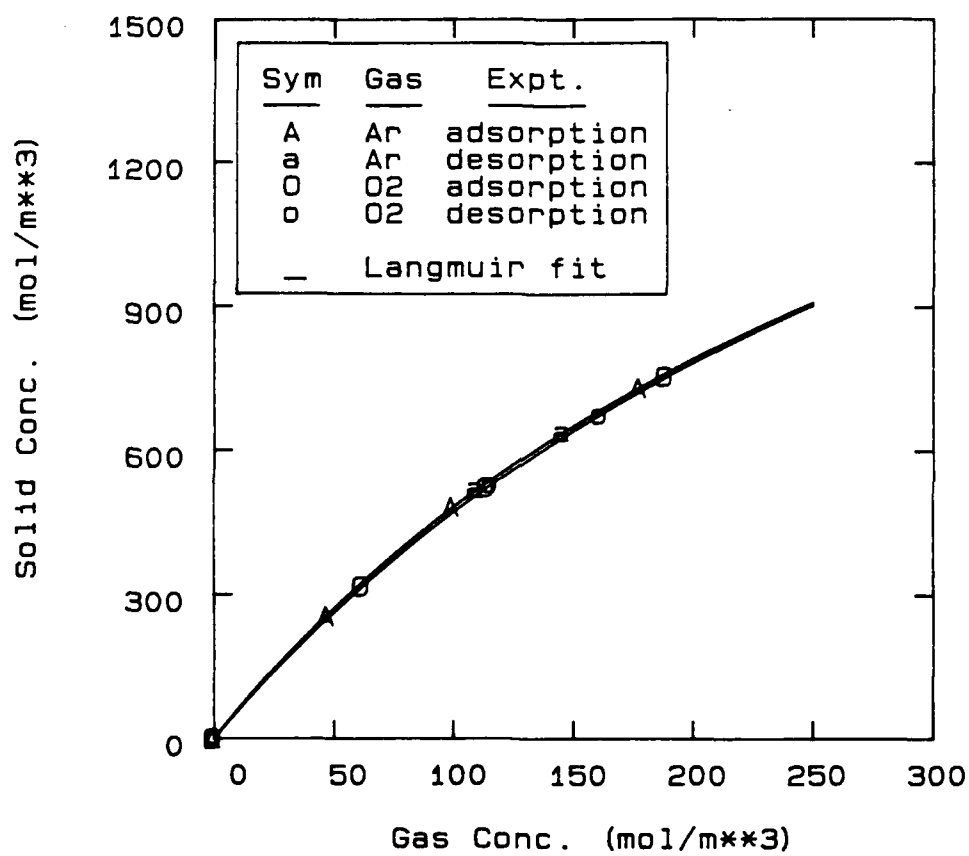
Figure 9. Adsorption of Argon and Oxygen on Sodium Mordenite at 0 C
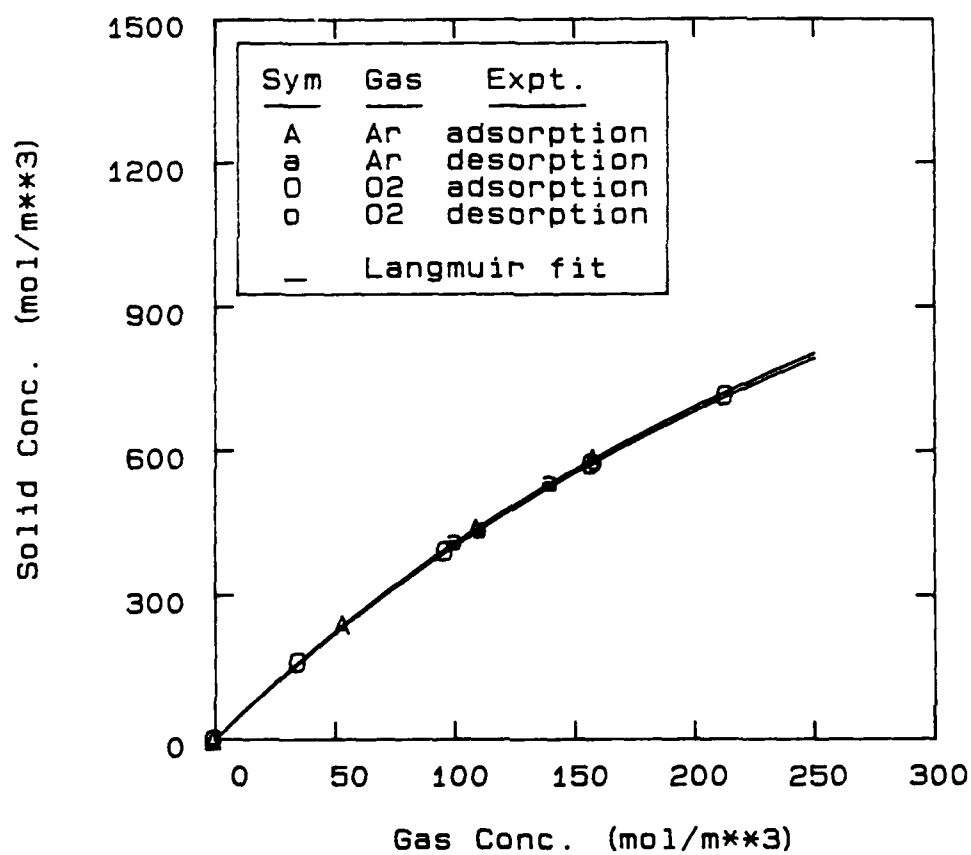
Figure 10. Adsorption of Argon and Oxygen on
Sodium Mordenite at 9.5 C
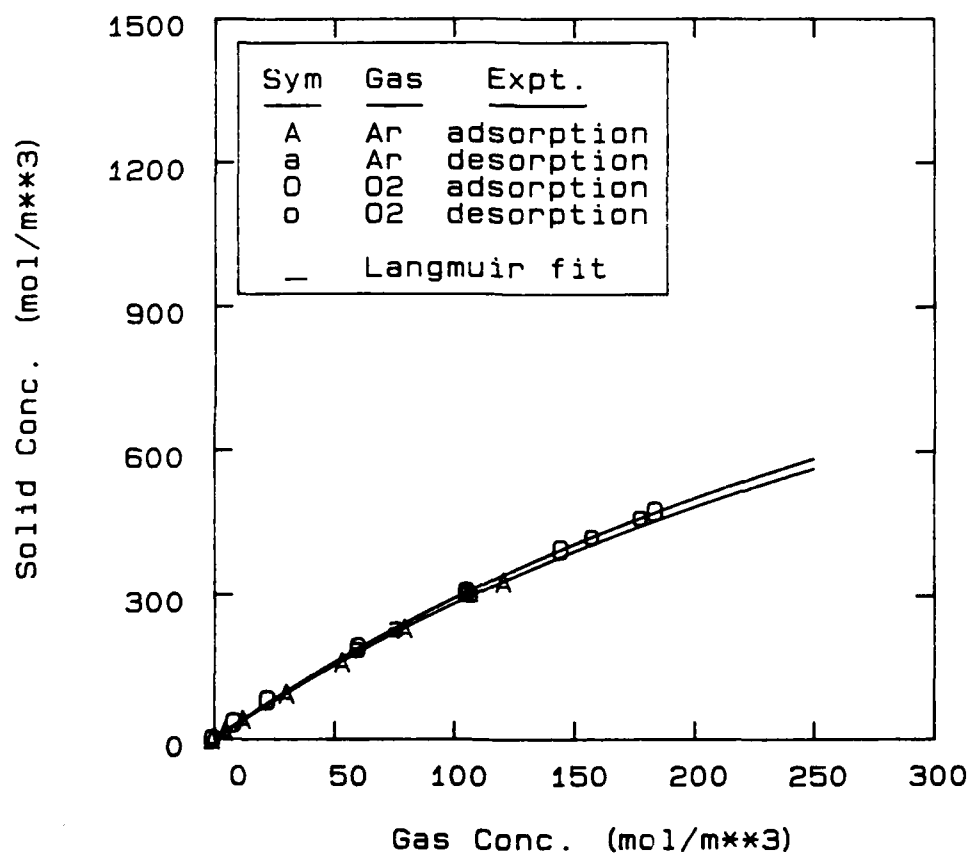
Figure 11. Adsorption of Argon and Oxygen on
Sodium Mordenite at 30 C
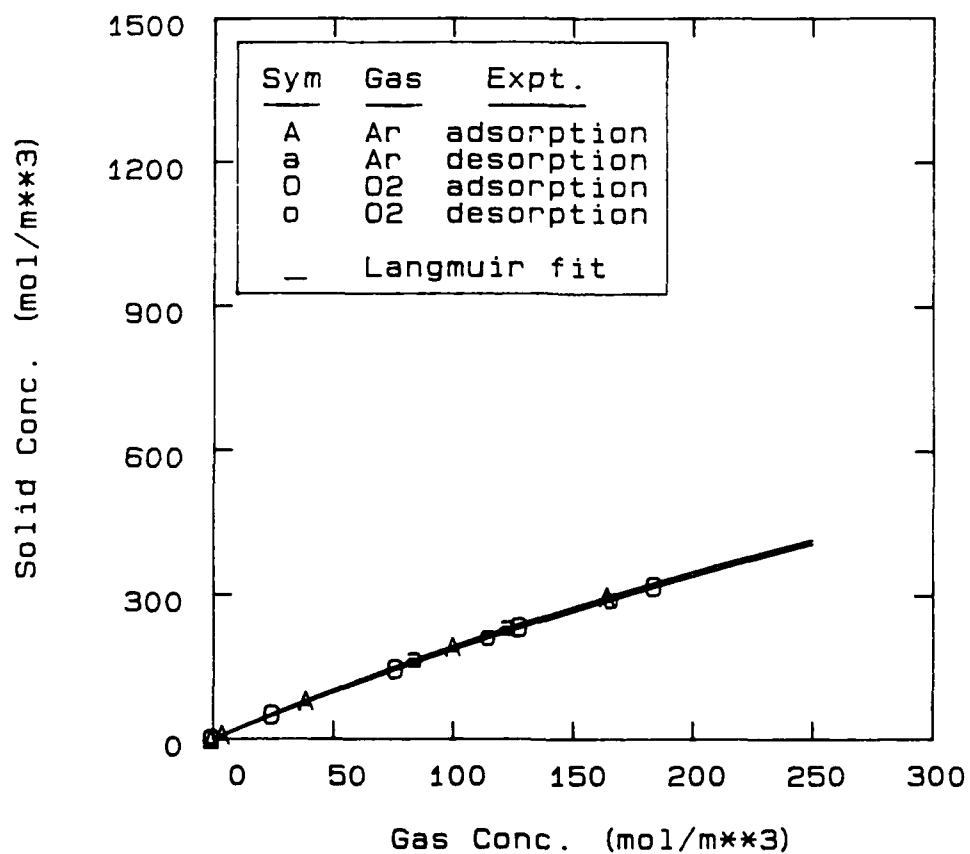
Figure 12. Adsorption of Argon and Oxygen on
Sodium Mordenite at 60 C
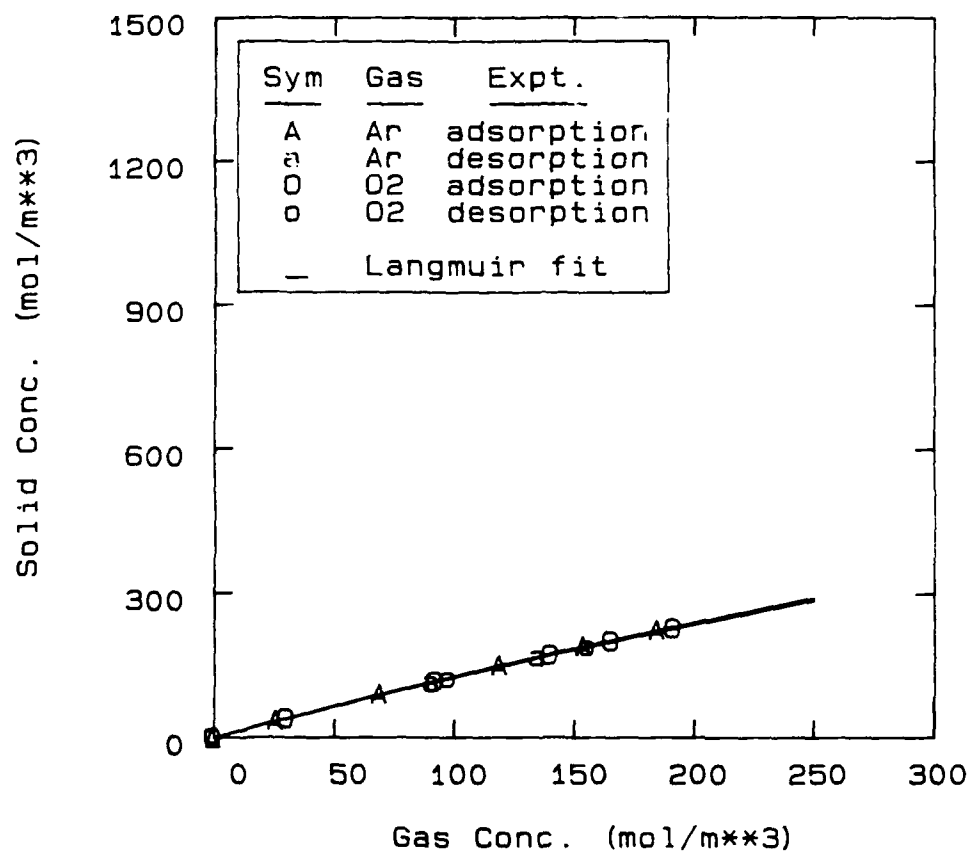
Figure 13. Adsorption of Argon and Oxygen on
Sodium Mordenite at 89 C
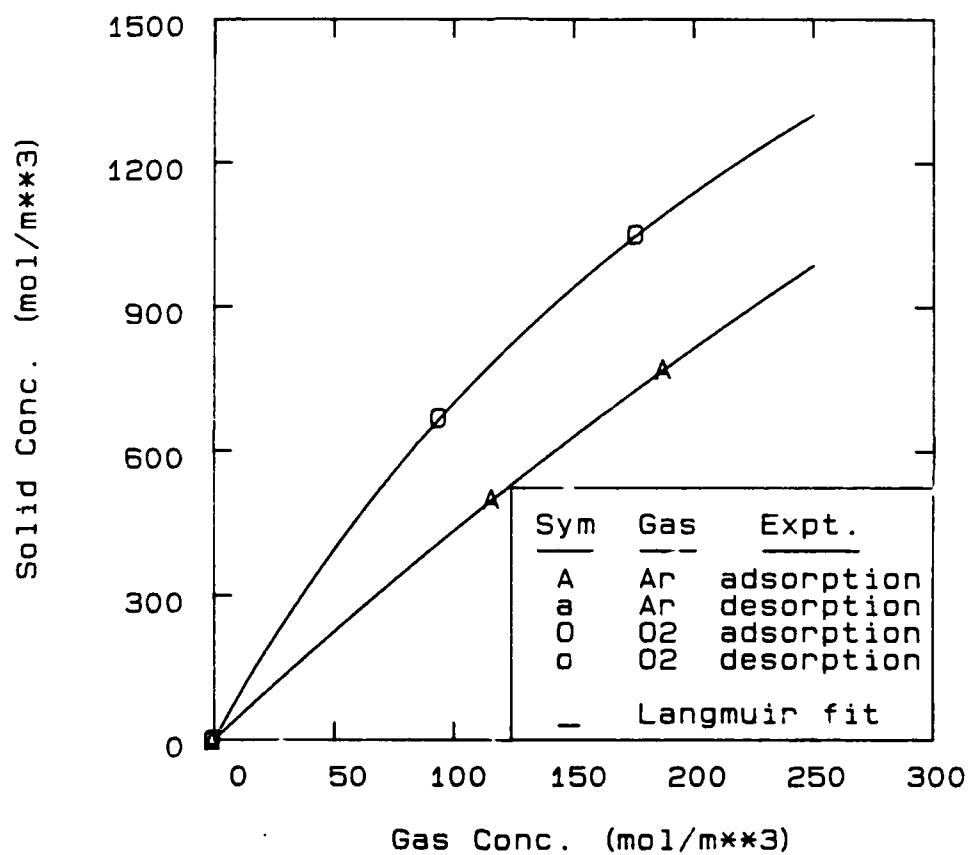
Figure 14. Adsorption of Argon and Oxygen on Batch
Exchanged Silver Mordenite at 0 C
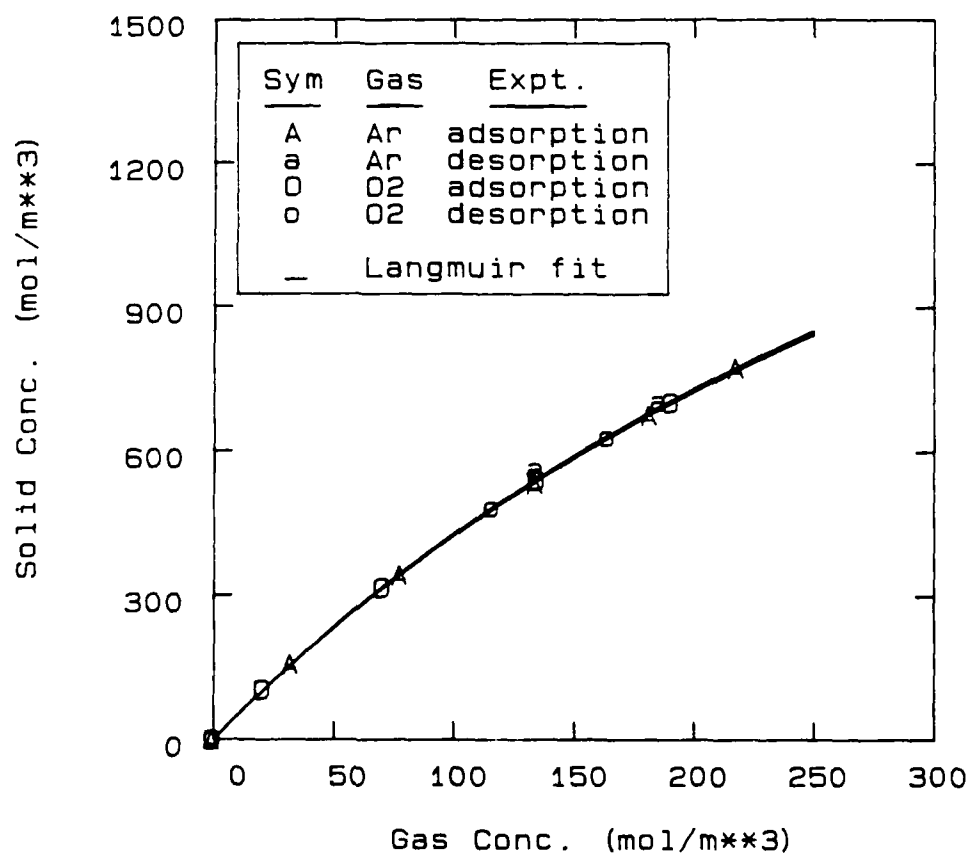
Figure 15. Adsorption of Argon and Oxygen on Batch
Exchanged Silver Mordenite at 30 C
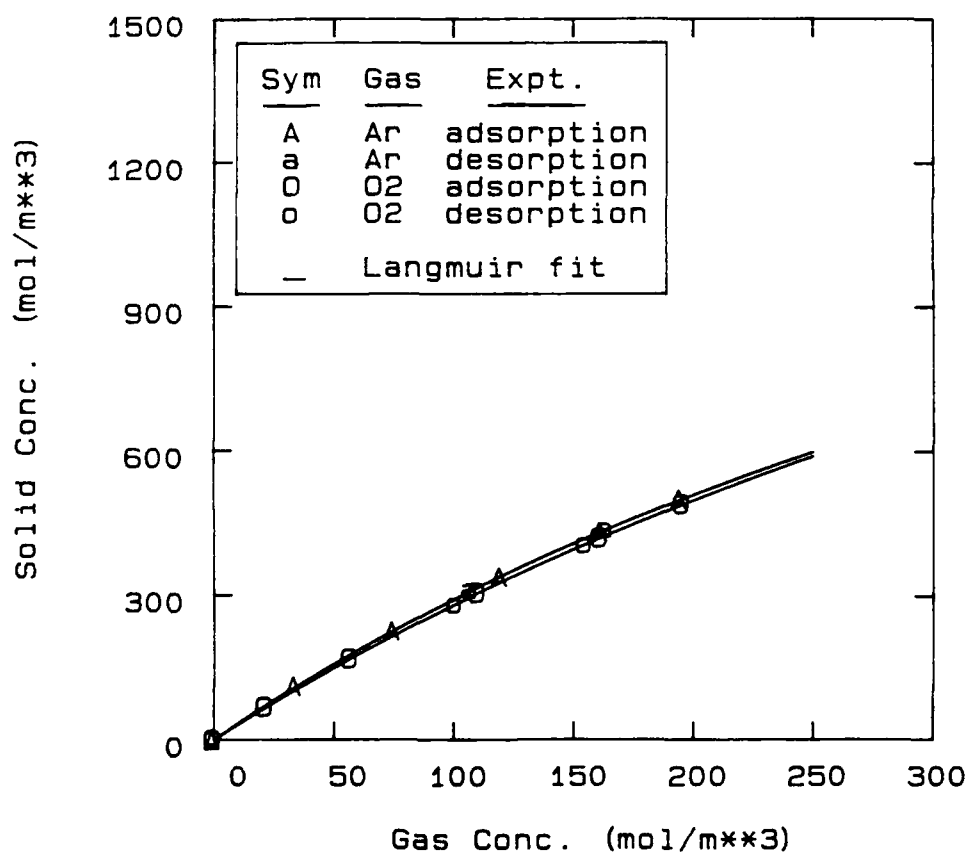
Figure 16. Adsorption of Argon and Oxygen on Batch Exchanged Silver Mordenite at 60 C
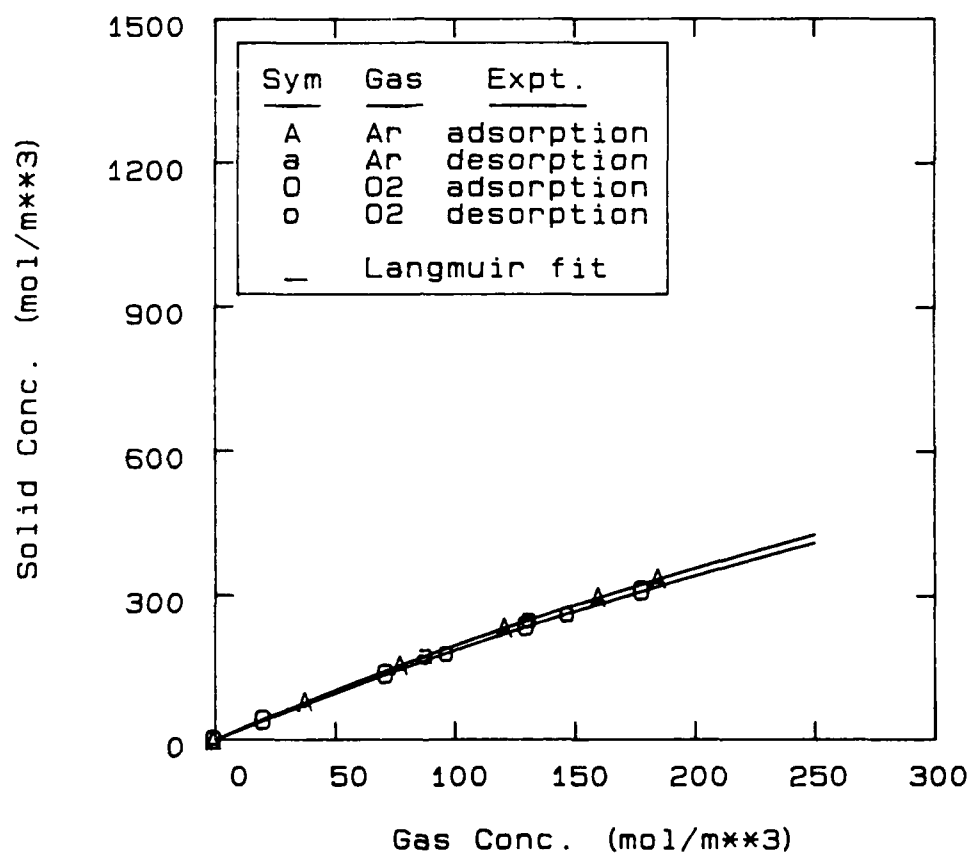
Figure 17. Adsorption of Argon and Oxygen on Batch
Exchanged Silver Mordenite at 89 C

of the adsorbent at these temperatures in an equilibrium-based PSA cycle.

Generally, the further apart the oxygen and argon curves are, the better the chance for a successful separation. As can be seen, the isotherms of argon and oxygen on silver mordenite show the potential for a successful separation. The isotherms on sodium mordenite, however, are practically identical. This means that sodium mordenite shows no selectivity between argon and oxygen. It was initially thought that the batch exchanged silver mordenite, which requires less time and resources to prepare, would show some selectivity. Although the adsorption of the gases increased considerably over that of the nonexchanged mordenite, no selectivity was shown except at 0 C, where the isotherms appear to show a reverse selectivity. However, as mentioned above, due to kinetic problems, operating at this temperature is impractical. Thus, the more thoroughly exchanged, higher concentrated silver mordenite is required for a successful separation.

Duplicate isotherms were performed of argon and oxygen on silver mordenite. These runs are compared in Figures 18 and 19. Comparing the variances gives F-ratios for the argon and oxygen isotherms as 0.752 and 1.489, respectively. The comparison F-ratio at a significance level of .05 is 3.48 [15], thus it cannot be rejected by the statistics that the variances of the duplicate runs are the same as the
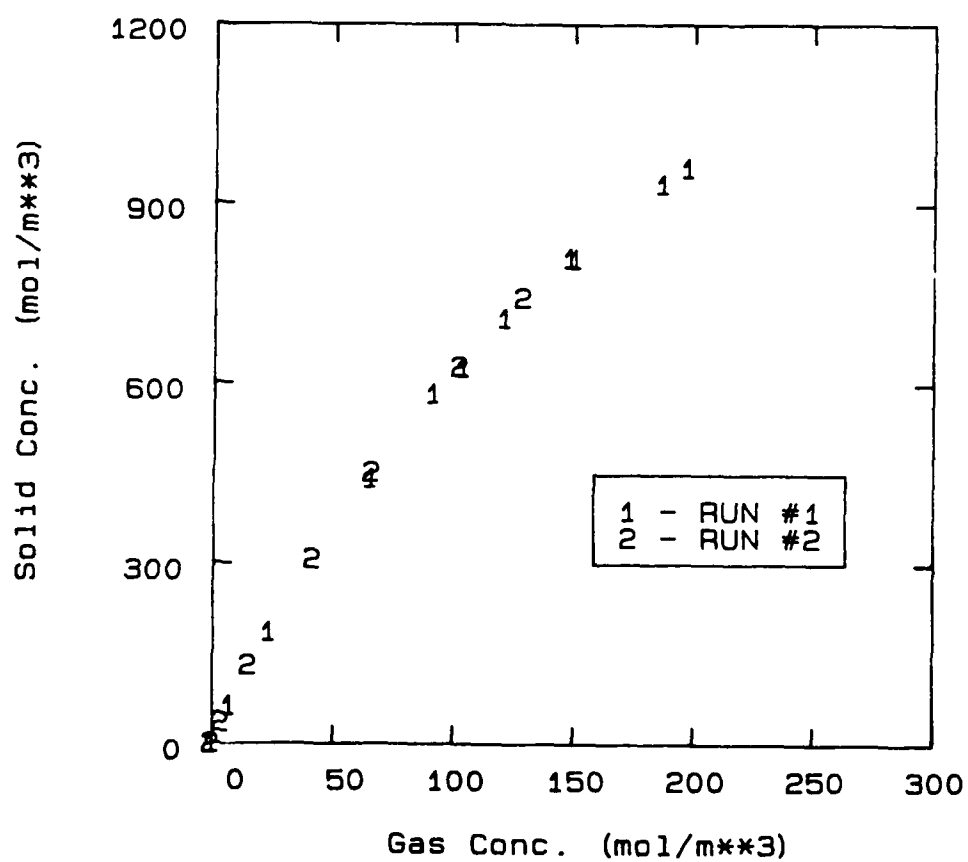
Figure 18. Comparison of runs: Argon on Silver
Mordenite at 30 C
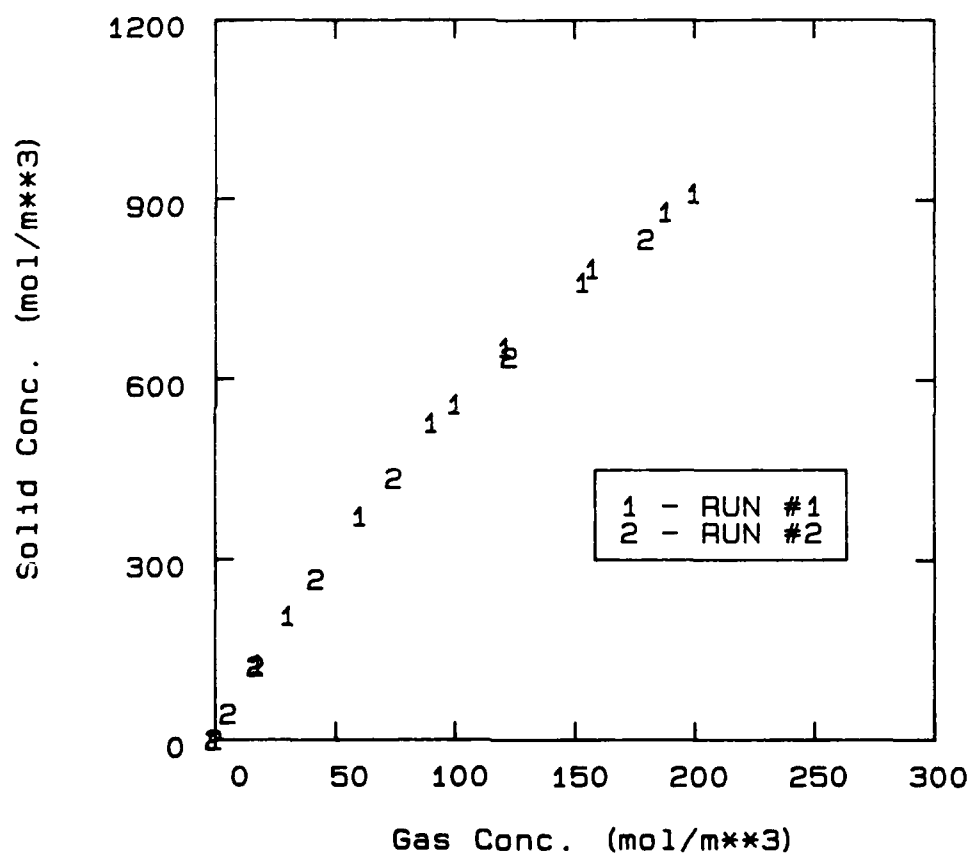
Figure 19. Comparison of runs: Oxygen on Silver
Mordenite at 30 C

original runs for both argon and oxygen. This means that the data were repeatable.

D.   Recovery Calculations

As described earlier, equilibrium theory, as modified by Kayser and Knaebel [12] for nonlinear isotherms, can be used to calculate a theoretical recovery for a given separation. In the case of the more strongly adsorbed component being very dilute in the feed, however, the theory may have a problem. A net recovery may be shown, though the plot of the isotherms shows no selectivity in the dilute range. Since argon is the more strongly adsorbed component, and the feed composition is 95% oxygen, and only 5% argon, this problem could occur in this analysis. This potential discrepancy must be resolved by PSA experiments.

In order to 'weed out' the nonselective adsorbents quantitatively, it is useful to look at a Henry's law selectivity, β_0. β_0 is the ratio of β_{A0}, as defined in equation (6), and β_{B0}, as defined similarly, except that m1 is the slope of the less strongly adsorbed component at y=0.

Table 3 is a list of β_0s for each adsorbent at each temperature. A β_0 of greater than, say, .92 to .95 would indicate that the adsorbent shows insignificant selectivity. On that basis, the high percentage exchanged silver mordenite is the only adsorbent that qualifies as being

Table 3: Selectivities of Adsorbents

Adsorbent T(deg C)	β_{A0}	β_{B0}	β_0
Silver Mordenite			
0	.10416	.11623	.89614
30	.16337	.18321	.89170
60	.24841	.27949	.88878
90	.38006	.42611	.89192
Sodium Mordenite			
0	.19777	.20440	.96758
10	.23358	.23689	.98601
30	.30904	.29998	1.0302
60	.41236	.42421	.97205
89	.52618	.52879	.99506
Batch Exchanged Silver Mordenite			
0	.25500	.14979	1.7024
30	.23520	.23699	.99248
60	.31831	.33246	.95744
90	.42275	.43846	.96417

selective. Its β_0 is almost constant with temperature; its average value is 0.892. β_0 for the other adsorbents varies up and down with temperature, which could mean that any difference between the two isotherms is due only to experimental error.

Equation (14) is then used to calculate the recoveries. These are tabulated at three different conditions in Tables 4 to 6. Specifically, Table 4 is the recovery at various temperatures for a pressure ratio of 6.0. The conditions chosen represent those possibly encountered during flight on an aircraft. The high pressure is 3.0 atm, which would be a typical operating condition, and the low pressure is 0.5 atm, which is the back pressure an on-board oxygen generating system may experience at an altitude of between 5000 and 6000 meters [22]. The second condition is a pressure ratio of 10,000, as shown in Table 5. This represents what would essentially be the maximum recovery as predicted by this theory, based on a conventional 4-step cycle. Table 6 compares the predicted recovery of 99.0% pure oxygen at a high pressure of 3.4 atm, and a back pressure of 0.98 atm, the conditions Miller [6] used in his work. As can be seen, the theory predicts that silver mordenite will show a better recovery than carbon molecular sieve by a factor of three-to-one.

Table 4:   Recoveries at a pressure ratio of 6.0

Silver Mordenite, y_{AF} = .05, y_{BF} = .95

Ph = 3.0 atm, Pl = 0.5 atm, y_B = .9999

Temperature (C)	0	30	60	90
Recovery	36.49%	25.74%	18.45%	12.64%

Table 5:   Recoveries at a pressure ratio of 10,000

Silver Mordenite, y_{AF} = .05, y_{BF} = .95

Ph = 10.0 atm, Pl = 0.001 atm, y_B = .9999

Temperature (C)	0	30	60	90
Recovery	60.77%	47.00%	34.25%	21.54%

Table 6: Comparison of Recoveries

Conditions from Miller [6]: $y_{AF} = .05$, $y_{BF} = .95$

Ph = 3.4 atm, Pl = .98 atm, $y_B = .99$

Silver Mordenite (30 C)   Carbon Molecular Sieve (24 C)[6]

Recovery	Silver Mordenite (30 C)	Carbon Molecular Sieve (24 C)[6]
Recovery	24.32%	7.0%

A breakdown of the three critical slopes described in Kayser and Knaebel [12] for each recovery calculation is in Appendix C. Using the Langmuir constants in Table 2, and equation (14), theoretical recoveries at any pressure ratio could be similarly calculated.

For the more common operating condition shown in Table 4, the predicted recovery is highest at 0 C. The recovery improves as temperature decreases. However, on top of the difficulties of running a process at 0 C, the kinetic problem mentioned earlier would prevent operation at this temperature. The trade-off between recovery and kinetics must be examined experimentally to determine the optimum operating temperature.

E. Isosteric Heats of Adsorption

As mentioned in Chapter II, the determination of the isotherms also allows for the determination of the isosteric heats of adsorption using equation (23). This allows the adsorbent samples to be further characterized. These heats are listed in Table 7. Figure 20 shows these data graphically. The heats of adsorption stay constant with, or increase slightly with loading.

Table 7:   Isosteric heats of adsorption

Adsorbent	Adsorbate	Loading cm^3(stp)/g ads	Heat of Adsorption kcal/mol
Silver Mordenite	Argon	1.0	3.62
		2.0	3.66
		3.0	3.70
		4.0	3.75
	Oxygen	1.0	3.74
		2.0	3.75
		3.0	3.75
		4.0	3.76
Low % Silver Mor.	Argon	1.0	3.19
		2.0	3.23
		3.0	3.28
		4.0	3.33
	Oxygen	1.0	3.38
		2.0	3.41
		3.0	3.45
		4.0	3.48
Sodium Mordenite	Argon	1.0	3.18
		2.0	3.23
		3.0	3.28
		4.0	3.33
	Oxygen	1.0	3.17
		2.0	3.21
		3.0	3.25
		4.0	3.27
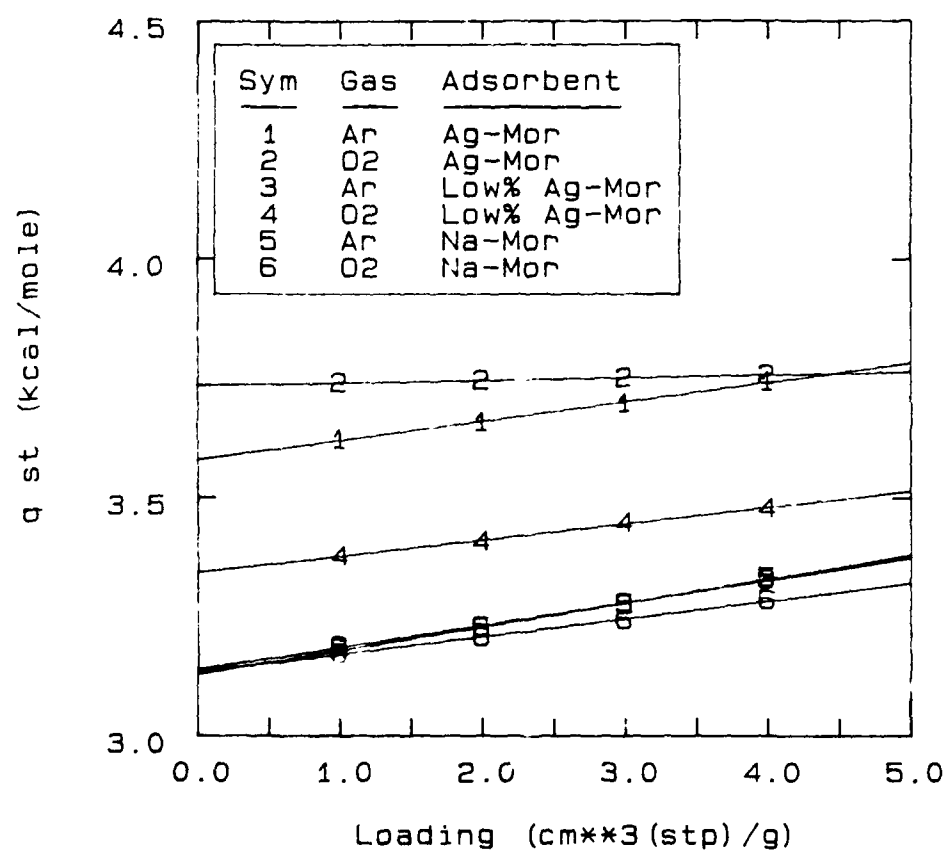
Figure 20. Isosteric Heats of Adsorption

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The goal of this research was to synthesize an adsorbent that could be used to separate argon from oxygen, yielding pure oxygen via a PSA system. As a potential adsorbent for this process, small pore mordenite in the silver cation exchanged form was examined. Three forms were used: the mordenite in its original (sodium) form, a batch-exchanged (low percent silver) form, and a column-exchanged (high percent silver) form. The equilibrium adsorption isotherms for argon and oxygen on these three forms at 0 C, 30 C, 60 C and 90 C were measured. The void fractions of the three adsorbents were also measured. The isotherms were compared qualitatively, in plots, and quantitatively, by a Henry's law selectivity. Only the high percent, more thoroughly exchanged silver mordenite showed selectivity towards argon.

The theoretical recoveries at typical PSA operating conditions, as well as a theoretical maximum recovery, were calculated. Although the predicted maximum recovery would occur at 0 C, the difficulties of operating at 0 C, and the slow kinetics described in Chapter IV, preclude this as

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being a viable operating temperature. Around 30 C would be
the recommended operating condition for an equilibrium-based
pressure swing adsorption system. To find the optimum
operating temperature would require the study of the
kinetics of the adsorption at various temperatures.

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APPENDICES

APPENDIX A

VOID FRACTION DETERMINATION

Table 8: Silver mordenite void fraction

Run	p_b (g/cm^3)	p_p (g/cm^3)	p_s (g/cm^3)	ϵ
1	.8580	2.3568	2.8027	
2	.8852	2.3664	2.8186	
3	.9015	2.3568	2.7576	
4	.9205	2.3659	2.7008	
5	.8899	2.3721		
6	.8967	2.3690		
7	.8967			
Average	.8926	2.3645	2.7699	0.6225
Std Dev.	.0189	.00636	.0528	

Note: In this and the following tables, data are grouped together for conciseness only. The individual runs are not related to runs in other columns. For example, p_b run 1 bears no relationship to p_p run 1.

Table 9:   Sodium mordenite void fraction

Run	p_b (g/cm^3)	p_p (g/cm^3)	p_s (g/cm^3)	ϵ
1	.8339	2.0987	2.1169	
2	.8284	2.1011	2.6615	
3	.8257	2.0963	2.5801	
4	.8325	2.0998	2.5138	
5	.8325	2.1021		
6		2.0998		
Average	.8306	2.0996	2.4487	0.6044
Std Dev.	.0034	.00204	.2418	

Table 10: Batch Exchanged Silver mordenite void fraction

Run	p_b (g/cm^3)	p_p (g/cm^3)	p_s (g/cm^3)	ϵ
1	.8362	2.1904	2.6310	
2	.8383	2.1871	2.5387	
3	.8417	2.1776	2.5657	
4	.8339	2.1987	2.5834	
5	.8417	2.1887		
6		2.1466		
Average	.8383	2.1815	2.5794	0.6157
Std Dev.	.0034	.01839	.0388	

Table 11:   Volume of System I

$V_A = V_B *$ Ratio, where Ratio $= \dfrac{(Peq-Psys)}{(Pa-Peq)}$

where these are measured in the same fashion as an adsorption isotherm, cell B is, however, empty.

Run	V_B (cc)	Ratio
1	154.07	1.07978
2	153.04	1.08062
3	153.05	1.08282
4	153.00	
5	153.72	
6	153.02	
7	152.87	
8	153.02	

Ave	153.22	1.08108
Std Dev	.4284	.00157

$V_A = 165.64$ cc

$V_B = 153.22$ cc

Table 12: Volume of System II

$V_A = V_B *$ Ratio, where Ratio $= \dfrac{(Peq-Psys)}{(Pa-Peq)}$

where these are measured in the same fashion as an adsorption isotherm, cell B is, however, empty.

Run	V_B (cc)	Ratio
1	157.38	1.05617
2	157.66	1.04898
3		1.04527
4		1.04586
5		1.04921

Ave	157.52	1.04910
Std Dev	.1980	.00434

$V_A = 165.25$ cc

$V_B = 157.52$ cc

APPENDIX B

ISOTHERM DATA AND RESULTS

Table 13: Argon on silver mordenite at 0 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.35	0.35	0.0000	0.0000
2	92.63	28.79	86.3403	809.6274
3	37.11	31.91	95.8122	863.6912
4	85.43	53.51	161.3872	1159.3539
5	94.27	71.28	215.3347	1339.5730
6	17.15	47.77	143.9612	1097.2117
7	17.66	35.66	107.1968	929.4427

The Langmuir constants are:

$K = 14.18240$ (mol/m^3)(solid)/(mol/m^3)(gas)

$r = 0.59716D-02$ (m^3/mol)(gas)

The standard error of estimate is:

0.34922D+01

Table 14: Oxygen on silver mordenite at 0 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.34	0.34	0.0000	0.0000
2	53.44	16.19	48.1186	483.4200
3	65.31	33.86	101.7626	828.1505
4	95.27	58.94	177.9023	1157.3285
5	41.98	51.66	155.8012	1078.4576
6	16.00	37.05	111.4470	888.8874

The Langmuir constants are:

$$K = 12.53820 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.52101D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.37676D+01$$

Table 15: Argon on silver mordenite at 30 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.57	0.57	0.0000	0.0000
2	8.96	3.25	7.3310	63.4329
3	20.78	9.17	23.5248	186.1349
4	51.26	24.64	65.8421	442.2012
5	60.01	38.64	104.1383	626.6969
6	79.28	55.68	150.7503	809.4017
7	94.64	72.78	197.5263	961.0937
8	64.48	68.97	187.1043	933.9037
9	36.96	54.87	148.5345	810.8196
10	31.53	44.95	121.3990	709.9948
11	18.39	34.05	91.5826	583.3348

The Langmuir constants are:

$K = 8.44450$ $(mol/m^3)(solid)/(mol/m^3)(gas)$

$r = 0.37205D-02$ $(m^3/mol)(gas)$

The standard error of estimate is:

$0.47344D+01$

Table 16: Oxygen on silver mordenite at 30 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.46	0.46	0.0000	0.0000
2	19.23	6.99	17.8624	125.5122
3	19.93	11.67	30.6643	206.5700
4	40.57	22.60	60.5627	372.9408
5	59.01	37.15	100.3634	558.6153
6	83.33	56.63	153.6498	762.6315
7	95.00	73.52	199.8515	910.5238
8	64.21	69.26	188.1985	879.6069
9	44.14	58.14	157.7803	784.7028
10	27.03	44.80	121.2895	653.9216
11	17.73	33.61	90.6799	527.3062

The Langmuir constants are:

$K = 7.35140$ (mol/m^3)(solid)/(mol/m^3)(gas)

$r = 0.30621D-02$ (m^3/mol)(gas)

The standard error of estimate is:

0.37672D+01

Table 17: Argon on silver mordenite at 60 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.81	0.81	0.0000	0.0000
2	7.52	3.37	6.3721	34.5275
3	24.69	11.93	27.6790	132.3369
4	37.96	22.78	54.6859	240.6134
5	57.19	37.58	91.5249	370.9857
6	77.73	55.41	135.9058	507.4338
7	95.73	73.81	181.7056	630.6496
8	51.76	63.61	156.3166	567.1059
9	39.29	52.58	128.8616	490.8747
10	22.97	39.44	96.1546	389.9853
11	19.26	30.70	74.3997	315.2151

The Langmuir constants are:

$K = 4.98934$ $(mol/m^3)(solid)/(mol/m^3)(gas)$

$r = 0.24196D-02$ $(m^3/mol)(gas)$

The standard error of estimate is:

0.20889D+01

Table 18: Oxygen on silver mordenite at 60 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.79	0.79	0.0000	0.0000
2	6.39	3.08	5.7001	24.5294
3	20.60	10.38	23.8706	97.4853
4	42.00	23.91	57.5484	219.2418
5	59.92	39.74	96.9511	346.1301
6	80.01	57.91	142.1784	474.9791
7	96.82	75.88	186.9078	587.9251
8	62.56	69.59	171.2513	553.1244
9	41.72	56.76	139.3159	471.0702
10	25.62	42.66	104.2194	372.8161
11	15.54	30.65	74.3250	279.7122

The Langmuir constants are:

K = 4.25105 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.18703D-02 (m^3/mol)(gas)

The standard error of estimate is:

0.18705D+01

Table 19: Argon on silver mordenite at 90 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.62	0.62	0.0000	0.0000
2	15.98	7.58	15.9150	44.3916
3	41.80	23.56	52.4555	131.1280
4	57.81	39.82	89.6362	211.1164
5	76.87	57.65	130.4070	291.4685
6	89.41	73.10	165.7356	356.0952
7	93.29	82.97	188.3047	395.9382
8	55.87	69.66	157.8695	344.0497
9	26.17	48.55	109.5986	254.3694
10	18.75	34.34	77.1055	186.3800

The Langmuir constants are:

$$K = 2.68983 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.15003D-02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.14353D+01$$

Table 20: Oxygen on silver mordenite at 90 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.83	0.83	0.0000	0.0000
2	15.91	8.05	16.5095	33.6571
3	30.81	18.87	41.2510	86.4314
4	65.42	41.27	92.4717	187.4327
5	73.21	56.82	128.0289	252.1065
6	92.75	74.46	168.3652	321.0763
7	93.15	83.69	189.4709	355.5660
8	75.49	79.58	180.0728	341.9850
9	48.09	64.01	144.4698	284.3560
10	21.94	43.44	97.4337	201.4333

The Langmuir constants are:

$$K = 2.22087 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.95212D-03 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.20004D+01$$

Table 21: Argon on sodium mordenite at 0 C

Pressures in psia, X and Y in mols/m³				
PT	PA	PEQ	X	Y
1	0.05	0.05	0.0000	0.0000
2	42.39	15.66	47.3900	255.5638
3	59.34	32.92	99.7892	483.0612
4	92.77	58.59	177.7202	731.5825
5	34.67	48.05	145.7220	641.0325
6	20.30	36.25	109.8987	522.6091

The Langmuir constants are:

$$K = 6.19725 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.28219D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.24984D\text{+}01$$

Table 22: Oxygen on sodium mordenite at 0 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.04	0.04	0.0000	0.0000
2	54.43	20.42	61.8712	353.9829
3	62.89	37.68	114.2704	584.5265
4	94.28	62.10	188.4065	843.4915
5	41.88	53.22	161.4479	756.2950
6	18.48	38.35	116.3044	593.3100

The Langmuir constants are:

K = 5.94683 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.25777D-02 (m^3/mol)(gas)

The standard error of estimate is:

0.75426D+02

Table 23: Argon on sodium mordenite at 9.5 C

Pressures in psia, X and Y in mols/m^3				
PT	PA	PEQ	X	Y
1	0.05	0.05	0.0000	0.0000
2	46.71	18.35	53.6892	239.0071
3	64.07	37.41	109.6082	439.0849
4	75.44	53.95	158.1339	584.7800
5	40.52	47.98	140.6189	537.2288
6	16.39	34.30	100.4840	414.4189

The Langmuir constants are:

$$K = 5.01313 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.22364D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.21205D+01$$

Table 24: Oxygen on sodium mordenite at 9.5 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.05	0.05	0.0000	0.0000
2	30.79	11.99	35.0300	160.9719
3	62.96	32.96	96.5526	392.4468
4	80.45	53.66	157.2831	573.0036
5	96.03	72.75	213.2901	715.3028
6	32.03	54.32	159.2194	581.0664
7	16.81	37.94	111.1631	439.3631

The Langmuir constants are:

$K = 4.92165$ (mol/m^3)(solid)/(mol/m^3)(gas)

$r = 0.21997D-02$ (m^3/mol)(gas)

The standard error of estimate is:

0.11560D+01

Table 25: Argon on sodium mordenite at 30 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.49	0.49	0.0000	0.0000
2	5.13	2.52	5.5529	17.2996
3	8.76	5.23	12.9660	41.1274
4	20.15	11.81	30.9652	95.2767
5	30.67	20.24	54.0250	160.5622
6	41.36	29.80	80.1758	230.2980
7	62.31	44.86	121.3716	327.9513
8	34.85	39.96	107.9679	305.2844
9	15.27	28.46	76.5103	232.8815
10	15.39	22.52	60.2618	190.3970

The Langmuir constants are:

K = 3.41589 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.20522D-02 (m^3/mol)(gas)

The standard error of estimate is:

•   0.50782D+01

Table 26: Oxygen on sodium mordenite at 30 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.63	0.63	0.0000	0.0000
2	8.47	3.88	8.8902	34.2967
3	15.83	9.00	22.8957	81.8939
4	39.94	22.75	60.5080	191.2327
5	59.07	39.34	105.8890	306.9437
6	69.99	53.69	145.1426	394.7420
7	83.91	68.07	184.4783	474.7976
8	63.72	65.94	178.6518	464.9651
9	50.54	58.58	158.5189	425.0699
10	18.25	39.65	106.7370	310.8918

The Langmuir constants are:

K = 3.56520 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.20939D-02 (m^3/mol)(gas)

The standard error of estimate is:

0.21702D+01

Table 27: Argon on sodium mordenite at 60 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.07	0.07	0.0000	0.0000
2	3.93	1.88	4.5053	9.1816
3	31.76	15.90	39.4027	80.0271
4	67.58	40.53	100.7097	192.7845
5	93.85	66.37	165.0285	298.1344
6	32.54	49.79	123.7589	236.0439
7	17.15	34.06	84.6051	169.2961

The Langmuir constants are:

$$K = 2.17725 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.12238D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

0.19974D+01

Table 28: Oxygen on sodium mordenite at 60 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.08	0.08	0.0000	0.0000
2	21.70	10.24	25.2894	50.8590
3	53.45	30.80	76.4657	145.9905
4	73.84	51.57	128.1647	233.2882
5	97.73	74.15	184.3689	319.1091
6	60.02	67.18	167.0198	294.3273
7	24.88	46.53	115.6195	214.6108

The Langmuir constants are:

K = 2.07370 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.10664D-02 (m^3/mol)(gas)

The standard error of estimate is:

0.68355D+00

Table 29:   Argon on sodium mordenite at 89 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.21	0.21	0.0000	0.0000
2	23.38	11.68	26.2640	36.4205
3	49.46	30.56	69.4953	91.6187
4	73.86	52.36	119.4128	151.0729
5	82.61	67.63	154.3780	191.6599
6	93.95	80.99	184.9697	225.2322
7	38.06	59.23	135.1437	169.7368
8	20.86	39.92	90.9278	116.8650

The Langmuir constants are:

K =   1.37575   (mol/m^3)(solid)/(mol/m^3)(gas)

r =   0.70640D-03   (m^3/mol)(gas)

The standard error of estimate is:

0.55103D+00

Table 30: Oxygen on sodium mordenite at 89 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.29	0.29	0.0000	0.0000
2	26.98	13.57	30.4085	40.3619
3	67.43	40.58	92.2559	116.8301
4	82.22	61.61	140.4103	172.4539
5	83.51	72.68	165.7583	201.4831
6	94.74	83.95	191.5643	227.9143
7	53.70	68.49	156.1641	191.8094
8	18.37	43.16	98.1635	125.2643

The Langmuir constants are:

$$K = 1.36144 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.73701D\text{-}03 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.76191D+00$$

Table 31:   Argon on batch exchanged silver mordenite at 0 C

	Pressures in psia, X and Y in mols/m^3			
PT	PA	PEQ	X	Y
1	0.23	0.23	0.0000	0.0000
2	90.65	38.59	116.4562	501.6313
3	92.45	62.13	187.9207	771.6533

The Langmuir constants are:

$$K = 4.68081 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.74456D\text{-}03 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.28346D\text{-}03$$

Table 32: Oxygen on batch exchanged silver mordenite at 0 C

PT	PA	PEQ	X	Y
	Pressures in psia, X and Y in mols/m^3			
1	0.34	0.34	0.0000	0.0000
2	84.96	31.44	94.4157	669.5638
3	96.36	58.48	176.5058	1050.6496

The Langmuir constants are:

$$K = 9.09396 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.29906D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.91746D\text{-}03$$

Table 33:   Argon on batch exchanged silver mordenite at 30 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.31	0.31	0.0000	0.0000
2	29.11	12.18	32.4697	157.0455
3	50.95	28.85	78.0695	342.5033
4	74.73	49.36	134.1735	532.5595
5	87.36	66.77	181.7975	674.0950
6	95.33	80.05	218.1242	773.1438
7	55.66	68.30	185.9828	703.9222
8	27.82	49.44	134.3923	564.9375

The Langmuir constants are:

$$K = 5.20958 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.21238D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.11309D+02$$

Table 34: Oxygen on batch exchanged silver mordenite at 30 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.28	0.28	0.0000	0.0000
2	19.01	7.95	20.9808	103.9983
3	50.67	26.11	70.6565	316.1799
4	78.84	49.57	134.8300	538.8270
5	93.99	70.02	190.7698	700.5693
6	49.25	60.32	164.2360	630.1239
7	22.02	42.86	116.4752	484.1857

The Langmuir constants are:

$$K = 5.15833 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.21154D-02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.16138D+01$$

Table 35: Argon on batch exchanged silver mordenite at 60 C

Pressures in psia, X and Y in mols/m^3				
PT	PA	PEQ	X	Y
1	0.70	0.70	0.0000	0.0000
2	30.95	14.29	33.8271	111.7292
3	49.95	30.81	74.9473	226.3640
4	68.96	48.81	119.7514	337.8425
5	83.83	65.58	161.4939	431.7378
6	93.05	78.87	194.5743	500.7592
7	53.37	66.44	163.6346	439.8699
8	19.25	43.83	107.3556	313.7603

The Langmuir constants are:

$$K = 3.43117 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$
$$r = 0.17199D\text{-}02 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

$$0.22104D+01$$

Table 36: Oxygen on batch exchanged silver mordenite at 60 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.42	0.42	0.0000	0.0000
2	19.68	9.15	21.7300	68.4939
3	39.89	23.33	57.0257	169.3390
4	68.90	44.75	110.3426	305.3158
5	87.43	65.18	161.1953	420.0272
6	93.63	78.97	195.5202	490.6264
7	45.55	62.75	155.1467	408.4117
8	17.28	41.04	101.1080	284.3038

The Langmuir constants are:

K = 3.21696 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.14443D-02 (m^3/mol)(gas)

The standard error of estimate is:

0.62093D+00

Table 37: Argon on batch exchanged silver mordenite at 89 C

PT	PA	PEQ	X	Y
	Pressures in psia, X and Y in mols/m^3			
1	0.44	0.44	0.0000	0.0000
2	34.93	17.12	38.1938	79.9179
3	52.61	34.49	77.9675	155.6627
4	73.05	53.51	121.5195	233.3230
5	87.65	70.50	160.4231	297.3579
6	92.20	81.37	185.3132	335.8316
7	34.75	58.03	131.8693	252.7674
8	19.81	39.12	88.5693	177.6067

The Langmuir constants are:

K = 2.18766 (mol/m^3)(solid)/(mol/m^3)(gas)

r = 0.11153D-02 (m^3/mol)(gas)

The standard error of estimate is:

0.96846D+00

Table 38: Oxygen on batch exchanged silver mordenite at 89 C

Pressures in psia, X and Y in mols/m^3

PT	PA	PEQ	X	Y
1	0.43	0.43	0.0000	0.0000
2	18.96	9.44	20.6311	41.4097
3	55.00	31.78	71.7851	137.3443
4	83.32	57.35	130.3352	236.5072
5	99.23	78.33	178.3751	310.7156
6	51.81	65.01	147.8750	264.8144
7	20.82	43.00	97.4766	182.5125

The Langmuir constants are:

$$K = 2.05187 \quad (mol/m^3)(solid)/(mol/m^3)(gas)$$

$$r = 0.99503D\text{-}03 \quad (m^3/mol)(gas)$$

The standard error of estimate is:

0.20669D+00

APPENDIX C

RECOVERY CALCULATIONS

Table 39: Product recovery using silver mordenite at 0 C

CONDITIONS: y_{BHP} = .9999 y_{BF} = 0.95 y_{AF} = 0.05

ϵ = 0.6225

Ph= 3.000 Pl= 0.500   m1= 14.18240

m2= 13.63740

m3= 4.44352

RECOVERY= 0.36490

Ph= 10.000 Pl= 0.001   m1= 14.18240

m2= 12.51522

m3= 1.17564

RECOVERY= 0.60765

Table 40: Product recovery using silver mordenite at 30 C

CONDITIONS: $y_{BHP} = .9999$ $y_{BF} = 0.95$ $y_{AF} = 0.05$

$e = 0.6225$

Ph=	3.000	Pl=	0.500	m1=	8.44450
				m2=	8.25921
				m3=	3.97456
				RECOVERY=	0.25741

Ph=	10.000	Pl=	0.001	m1=	8.44450
				m2=	7.85694
				m3=	1.51902
				RECOVERY=	0.47004

Table 41: Product recovery using silver mordenite at 60 C

CONDITIONS: $y_{BHP} = .9999$ $y_{BF} = 0.95$ $y_{AF} = 0.05$

$\epsilon = 0.6225$

Ph=	3.000	Pl=	0.500	m1=	4.98934
				m2=	4.92397
				m3=	2.95166
				RECOVERY=	0.18445

Ph=	10.000	Pl=	0.001	m1=	4.98934
				m2=	4.77790
				m3=	1.52990
				RECOVERY=	0.34252

Table 42: Product recovery using silver mordenite at 90 C

CONDITIONS: y_{BHP} = .9999 y_{BF} = 0.95 y_{AF} = 0.05

ϵ = 0.6225

Ph=	3.000 Pl=	0.500	m1=	2.68983
			m2=	2.66964
			m3=	1.85705
		RECOVERY=		0.12642

Ph=	10.000 Pl=	0.001	m1=	2.68983
			m2=	2.62369
			m3=	1.29036
		RECOVERY=		0.21543

Table 43: Comparison of recoveries data

CONDITIONS: $y_{BHP} = .99$ $y_{BF} = 0.95$ $y_{AF} = 0.05$

$\epsilon = 0.6225$ Temp = 30 C

Ph=   3.400 Pl=   0.980   m1=   8.44450

m2=   8.23511

m3=   3.71905

RECOVERY=   0.24321

APPENDIX D

COMPUTER PROGRAM LISTINGS

```fortran
C  THE PURPOSE OF THIS FILE IS TO EVALUATE DATA GATHERED
FROM
C  ISOTHERM EXPERIMENTS
      PROGRAM ISOTHERM
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER GTTL*40
      DIMENSION PA(30),PEQ(30),XMOL(30),YMOL(30)
      OPEN(UNIT=4,FILE='ISO.DAT',STATUS='OLD',READONLY)
      DO KNTR=1,2
      READ(4,4)TC
      READ(4,6)N,NDES
      NADS=N-NDES
   1 FORMAT(I5)
   2 FORMAT(I5,2X,F6.2,2X,F6.2,2X,F10.4,2X,F10.4)
   3    FORMAT(2D10.5)
   4 FORMAT(D10.5)
   5    FORMAT(2D13.5)
   6 FORMAT(2I3)
   7 FORMAT('    ')
      DO I=1,N
        READ(4,3)PA(I),PEQ(I)
      ENDDO
      READ(4,306)GTTL
C
C   SET UP OUTPUT SCHEME
C
      IF(KNTR.EQ.1)THEN
        IOUT=7
        OPEN(UNIT=3,FILE='JUNKA.DAT',STATUS='NEW')
        OPEN(UNIT=9,FILE='JUNK1A.DAT',STATUS='NEW')
        OPEN(UNIT=2,FILE='JUNK2A.DAT',STATUS='NEW')
      ELSE
        CLOSE(UNIT=2)
        CLOSE(UNIT=3)
        CLOSE(UNIT=9)
        IOUT=8
        OPEN(UNIT=3,FILE='JUNKB.DAT',STATUS='NEW')
        OPEN(UNIT=9,FILE='JUNK1B.DAT',STATUS='NEW')
        OPEN(UNIT=2,FILE='JUNK2B.DAT',STATUS='NEW')
      ENDIF
C
C   ENTER IN TEMP IN DEG C
C
      ZERO=0.0D0
C
C   AG-MOR PARAMETERS IN SYSTEM I
C
C   WT=61.70D0
C   PARTDENS=2.3645D0
C   EPS=.6225D0
C   VA=165.64D0
C   VB=153.22D0
```

```
C
C   NA-MOR PARAMETERS IN SYSTEM II
C
C     WT=59.96D0
C     PARTDENS=2.0996D0
C     EPS=.6044D0
C     VA=165.25D0
C     VB=157.52D0
C
C  NOTE: NA-MOR AT 30 C WAS IN SYSTEM I
C     WT=59.30D0
C
C
C   LO% AG-MOR PARAMETERS IN SYSTEM I
C
      WT=47.21D0
      PARTDENS=2.1815D0
      EPS=.6157D0
      VA=165.64D0
      VB=153.22D0
C
C
      TEMP=TC+273.15D0
      RGAS=82.057D0
      PCONV=14.696D0
      GASVOL=VA+VB-WT/PARTDENS
      SOLVOL=WT/PARTDENS
      GMOLS=0.0D0
      SMOLS=0.0D0
      DO K=2,N
        TMOLS=((PA(K)-PEQ(K-1))*VA/(PCONV*RGAS*TEMP))
           GMOLINC=(PEQ(K)-PEQ(K-1))*GASVOL/(PCONV*RGAS*TEMP)
        SMOLINC=TMOLS-GMOLINC
        GMOLS=GMOLS+GMOLINC
        SMOLS=SMOLS+SMOLINC
        XMOL(K)=(GMOLS/GASVOL)*1.0D6
        YMOL(K)=(SMOLS/SOLVOL)*1.0D6
      ENDDO
      XMOL(1)=0.0D0
      YMOL(1)=0.0D0
   10      FORMAT('    PT    PA    PEQ        X
     X   Y')
   11 FORMAT('    TABLE')
   12 FORMAT('    Pressures in psia, X and Y in mols/m**3')
      WRITE(IOUT,11)
      WRITE(IOUT,7)
      WRITE(IOUT,307)GTTL
      WRITE(IOUT,7)
      WRITE(IOUT,12)
      WRITE(IOUT,7)
      WRITE(IOUT,10)
      DO I=1,N
```

```
      WRITE(IOUT,2)I,PA(I),PEQ(I),XMOL(I),YMOL(I)
      WRITE(3,5)XMOL(I),YMOL(I)
   ENDDO
   DO I=1,NADS
      WRITE(9,5)XMOL(I),YMOL(I)
   ENDDO
   DO I=NADS+1,N
      WRITE(2,5)XMOL(I),YMOL(I)
   ENDDO
306 FORMAT(A)
307 FORMAT('        ',A)
   ENDDO
   STOP
   END
```

```
C   THE PURPOSE OF THIS FILE IS TO GENERATE A FILE WITH
C   THE FUNCTION GENERATED FROM 'BOX' AND ADD SOME INFO
C   TO THE OUTPUT FILES
      PROGRAM PLOTGEN
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 XP(1000),YP(1000)
      CHARACTER ATTL*40,BTTL*40
      DIMENSION XA(15),YA(15),XB(15),YB(15)
      DATA RGAS,TEMP/82.057D-6,273.15D0/
    1 FORMAT('   ENTER KA,RA')
    2 FORMAT('   ENTER KB,RB')
    3 FORMAT(4D14.6)
    4 FORMAT('   ENTER TEMP')
    5    FORMAT(2D13.5)
    6    FORMAT(D13.5)
      WRITE(6,1)
      READ(5,5)XKA,XRA
      WRITE(6,2)
      READ(5,5)XKB,XRB
      WRITE(6,4)
      READ(5,6)XT

 OPEN(UNIT=1,FILE='WPLANG.DAT',STATUS='OLD',ACCESS='APPEND')
      WRITE(1,3)XKA,XRA,XKB,XRB
      CLOSE(UNIT=1)
C
C     CALCULATE THE SMOOTH CURVE POINTS
C
      XMAX=250.0
      XINC=XMAX/500.0D0
      DO KNTR=1,2
        IF(KNTR.EQ.1)THEN
          XK=XKA
          XR=XRA
          OPEN(UNIT=3,FILE='JUNK3A.DAT',STATUS='NEW')
        ELSE
          CLOSE(UNIT=3)
          XK=XKB
          XR=XRB
          OPEN(UNIT=3,FILE='JUNK3B.DAT',STATUS='NEW')
        ENDIF
      PYRT=0.0D0
      DO I=1,501
        XP(I)=PYRT
        CALL FUNCT(PYRT,XK,XR,FUN)
        YP(I)=FUN
        PYRT=PYRT+XINC
        WRITE(3,5)XP(I),YP(I)
      ENDDO
      ENDDO
      CLOSE(UNIT=3)
C THIS SECTION IS FOR ADDING INFO TO THE OUTPUT FILES
```

```
OPEN(UNIT=7,FILE='FOR007.DAT',STATUS='OLD',ACCESS='APPEND')

OPEN(UNIT=8,FILE='FOR008.DAT',STATUS='OLD',ACCESS='APPEND')
     OPEN(UNIT=1,FILE='JUNK1A.DAT',STATUS='OLD',READONLY)
     OPEN(UNIT=2,FILE='JUNK2A.DAT',STATUS='OLD',READONLY)
     OPEN(UNIT=3,FILE='JUNK1B.DAT',STATUS='OLD',READONLY)
     OPEN(UNIT=4,FILE='JUNK2B.DAT',STATUS='OLD',READONLY)
C
C   THIS PART CALCULATES THE STANDARD ERROR OF ESTIMATION
C
     DO I=1,20
        XA(I)=0.0D0
        YA(I)=0.0D0
        XB(I)=0.0D0
        YB(I)=0.0D0
     ENDDO
     ICNT=1
     DO I=1,15
        READ(1,5,END=50)XA(I),YA(I)
        ICNT=ICNT+1
     ENDDO
  50 CLOSE(UNIT=1)
     DO I=ICNT,15
        READ(2,5,END=51)XA(I),YA(I)
        ICNT=ICNT+1
     ENDDO
  51 CLOSE(UNIT=2)
     NA=ICNT-1
     ICNT=1
     DO I=1,15
        READ(3,5,END=52)XB(I),YB(I)
        ICNT=ICNT+1
     ENDDO
  52 CLOSE(UNIT=3)
     DO I=ICNT,15
        READ(4,5,END=53)XB(I),YB(I)
        ICNT=ICNT+1
     ENDDO
  53 CLOSE(UNIT=4)
     NB=ICNT-1
     ESSA=0.0D0
     ESSB=0.0D0
     DO I=1,NA
        PYRT=XA(I)
        CALL FUNCT(PYRT,XKA,XRA,FUN)
        ESSA=ESSA+(YA(I)-FUN)**2
     ENDDO
     DO I=1,NB
        PYRT=XB(I)
        CALL FUNCT(PYRT,XKB,XRB,FUN)
        ESSB=ESSB+(YB(I)-FUN)**2
```

```
      ENDDO
      SIGA=DSQRT(ESSA/(DFLOAT(NA-2)))
      SIGB=DSQRT(ESSB/(DFLOAT(NB-2)))
  99      FORMAT('    ')
 100      FORMAT('  The Langmuir constants are: ')
 101      FORMAT(5X,'      K = ',F8.5,'
(mol/m3)(solid)/(mol/m3)(gas)')
 102      FORMAT(5X,'      r =',D13.5,'  (m3/mol)(gas)')
 103      FORMAT('  The standard error of estimate is:')
 104      FORMAT(15X,D12.5)
      WRITE(7,99)
      WRITE(7,100)
      WRITE(7,101)XKA
      WRITE(7,102)XRA
      WRITE(7,99)
      WRITE(7,103)
      WRITE(7,104),SIGA
      WRITE(8,99)
      WRITE(8,100)
      WRITE(8,101)XKB
      WRITE(8,102)XRB
      WRITE(8,99)
      WRITE(8,103)
      WRITE(8,104),SIGB

C
C         CALCULATION OF RECOVERY AT TWO CONDITIONS
C
 204 FORMAT(A)
      OPEN(UNIT=4,FILE='RECOV.DAT',STATUS='NEW')
      REWIND 7
      DO I=1,3
      READ(7,204)ATTL
      ENDDO
      CLOSE (UNIT=7)
      REWIND 8
      DO I=1,3
      READ(8,204)BTTL
      ENDDO
      CLOSE (UNIT=8)
C
C   FOR AG-MOR, HI%
C     EPS=.6225D0
C
C   FOR NA-MOR
C     EPS=.6044D0
C   FOR AG-MOR, LO%
      EPS=.6157D0
C
      YAF=.05D0
      YBF=.95D0
      YBHP=.9999D0
```

```
      T=XT
  210 FORMAT('   TABLE')
      WRITE(4,210)
      WRITE(4,99)
      WRITE(4,204)ATTL
      WRITE(4,204)BTTL
      WRITE(4,99)
  211 FORMAT('  CONDITIONS:   YBHP=',F4.2,'   YBF=',F4.2,'
YAF=',
     X   F4.2)
  212 FORMAT('                        EPS=',F6.4)
      WRITE(4,211)YBHP,YBF,YAF
      WRITE(4,212)EPS
      ONE=1.0D0
      T=T+TEMP
      BA0=ONE/(ONE+((ONE-EPS)/EPS)*XKA)
      PH=3.0D0
      PL=.50D0
        DO I=1,2
      PYRT=PH*YAF/(RGAS*T)
      CALL FUNCT(PYRT,XKA,XRA,FUN)
      XM2=FUN/PYRT
      PYRT1=PH*YBHP/(RGAS*T)
      PYRT2=PH*YBF/(RGAS*T)
      CALL FUNCT(PYRT1,XKB,XRB,FUN1)
      CALL FUNCT(PYRT2,XKB,XRB,FUN2)
      XM3=(FUN1-FUN2)/(PYRT1-PYRT2)
      THETAB=ONE/(ONE+((ONE-EPS)/EPS)*XM3)
      THETAA=ONE/(ONE+((ONE-EPS)/EPS)*XM2)
      THETA=THETAA/THETAB
C
      R1=(ONE+(THETA-ONE)*YAF)/THETAA
      R2=(PL/PH)*((BA0-ONE)/BA0)-1
C
C     YBH AND YBL BOTH = 1
C
      PYRT3=PH/(RGAS*T)
      PYRT4=PL/(RGAS*T)
      CALL FUNCT(PYRT3,XKB,XRB,FBH)
      CALL FUNCT(PYRT4,XKB,XRB,FBL)
      R3=-((ONE-EPS)/EPS)*((RGAS*T)/PH)*(FBH-FBL)
      R4=(ONE-YAF)/THETAA
      REC=(R1+R2+R3)/R4
  215 FORMAT(' PH= ',F7.3,' PL= ',F7.3,'          M1= ',F10.5)
  216 FORMAT('                                  M2= ',F10.5)
  217 FORMAT('                                  M3= ',F10.5)
  218 FORMAT('                              RECOVERY= ',F10.5)
      WRITE(4,99)
      WRITE(4,215)PH,PL,XKA
      WRITE(4,216)XM2
      WRITE(4,217)XM3
      WRITE(4,218)REC
```

```
PH=10.0D0
PL=.001D0
  ENDDO
STOP
END


SUBROUTINE FUNCT(PYRT,XK,XR,FUN)
IMPLICIT REAL*8(A-H,O-Z)
FUN=(XK*PYRT)/(1.0D0+XR*PYRT)
RETURN
END
```

```
      PROGRAM HEAT
C     CALCULATION OF ISOSTERIC HEAT OF ADSORPTION, AG-MOR
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION XKA(4),XRA(4),XKO(4),XRO(4),T(4),DELH(4)
      DIMENSION XLDG(4),XLP(4,4),XINVT(4),X(4),Z(4)
      DATA RGAS,TEMP/82.057D-6,273.15D0/
      DATA T(1),T(2),T(3),T(4)/0.0D0,30.0D0,60.0D0,90.0D0/
      DATA XKA(1),XRA(1)/14.1824D0,.597161D-2/
      DATA XKO(1),XRO(1)/12.5382D0,.521006D-2/
      DATA XKA(2),XRA(2)/8.44450D0,.372051D-2/
      DATA XKO(2),XRO(2)/7.35140D0,.306207D-2/
      DATA XKA(3),XRA(3)/4.98934D0,.241958D-2/
      DATA XKO(3),XRO(3)/4.25105D0,.187029D-2/
      DATA XKA(4),XRA(4)/2.68983D0,.150029D-2/
      DATA XKO(4),XRO(4)/2.22087D0,.952117D-3/
   1  FORMAT(2E10.5)
      OPEN(UNIT=7,FILE='HEAT.DAT',STATUS='NEW')
      XLDG(1)=1.0D0
      XLDG(2)=2.0D0
      XLDG(3)=3.0D0
      XLDG(4)=4.0D0
      RHOPART=2.3645
      STPMOL=.02241387D0
      DO I=1,4
        TEM=T(I)+TEMP
        XINVT(I)=1.0D0/TEM
        X(I)=XINVT(I)
      ENDDO
      DO K=1,4
        DO I=1,4
          Y=XLDG(K)*RHOPART/STPMOL
          P=RGAS*TEM*(Y/(XKA(I)-Y*XRA(I)))
          XLP(K,I)=DLOG(P)
          Z(I)=XLP(K,I)
        ENDDO
        CALL SLOPE (X,Z,D)
        DELH(K)=-.0019870D0*D
      ENDDO
   2  FORMAT ('   ARGON ON AG-MOR')
   3  FORMAT ('               1/TEMP ',4E12.5,' DEL Hst
     (kcal/mol)')
   4  FORMAT ('   LN(P) AT LOADING')
   5  FORMAT (1X,F3.1,'cm**3(stp)/g)',2X,5E12.5)
   6  FORMAT ('   OXYGEN ON AG-MOR')
      WRITE(7,2)
      WRITE(7,3)(XINVT(I),I=1,4)
      WRITE(7,4)
      DO J=1,4
        WRITE(7,5)XLDG(J),(XLP(J,I),I=1,4),DELH(J)
      ENDDO
      DO K=1,4
        DO I=1,4
```

```
            Y=XLDG(K)*RHOPART/STPMOL
            P=RGAS*TEM*(Y/(XKO(I)-Y*XRO(I)))
            XLP(K,I)=DLOG(P)
            Z(I)=XLP(K,I)
          ENDDO
          CALL SLOPE (X,Z,D)
          DELH(K)=-.0019870D0*D
        ENDDO
        WRITE(7,6)
        WRITE(7,3)(XINVT(I),I=1,4)
        WRITE(7,4)
        DO J=1,4
          WRITE(7,5)XLDG(J),(XLP(J,I),I=1,4),DELH(J)
        ENDDO
        STOP
        END

        SUBROUTINE SLOPE(X,Y,D)
C       THIS SECTION DOES A LINEAR LEAST SQUARES FIT FOR
INPUTTED DATA
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION X(4),Y(4)
        ZERO=0.0D0
C   MODEL 1--Y=B0+B1*X
        N=4
        SX=ZERO
        SY=ZERO
        SXX=ZERO
        SXY=ZERO
        DO J=1,N
          SX=SX+X(J)
          SY=SY+Y(J)
          SXX=SXX+(X(J)**2)
          SXY=SXY+(X(J)*Y(J))
        ENDDO
        DENOM=DFLOAT(N)*SXX-SX**2
        SLP=(DFLOAT(N)*SXY-SX*SY)/DENOM
        YINTC=(SY*SXX-SX*SXY)/DENOM
        B0=YINTC
        B1=SLP
        D=B1
        RETURN
        END
```

APPENDIX E

EQUIPMENT LISTING

Gases:
Argon, AGA Gas Inc, UN1006, purified 69695
Oxygen, Union Carbide, Linde Div, UN1072, zero grade
Helium, Union Carbide, Linde Div, UN1046, research grade
(for use in solid density measurements)

Pressure Regulators:
National Cylinder Gas, model N1602 (oxygen)
Matheson, model 9-590 (argon,nitrogen,helium)

Isotherm Baths:
2 large baths
Haake E3 temperature controller (+/- .005 deg C accuracy)
Grenier and Co., 3001, air driven mixer

Temperature Measurements:
Fluke 8840A multimeter
Dewar flask (cold junction)
2 type K thermocouples

Pressure Measurements:
2 Sensotec model A-S1713 10 (0-100 psia +/- 0.01 psia)
pressure transducers, #134663 and #134644
Sensotec SA-series, SA-10D, #84032 with channel select

Column Exchange:
1" Kimax beaded glass, 24" long
3" to 1" Kimax reducer beaded glass
3" Kimax T-beaded glass
Cole Parmer paristaltic pump, 7553-00

Heating:
Variac type 116, Superior Electric Co.
1/2 " heating tape, 3' long